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AFRL-ML-TY-TR-1998-4534



DETERMINATION/VALIDATION OF TECHNOLOGIES
FOR TREATMENT/RECYCLE OF CONTAMINATED
SLUDGES: PHASE I – SITE/SLUDGE
CHARACTERIZATION AND LABORATORY TESTING

ORON SCHUSS, BRUCE MONZYK, DALE FOLSOM, NICK CONKLE
AND ROBERT LITT
BATTELLE
505 KING AVENUE
COLUMBUS OH 43201-2693

PAMELA M. FRANKLIN AND DEAN WOLBACH
ARCADIS GERAGHTY & MILLER, INC.
555 CLYDE AVENUE
MOUNTAIN VIEW CA 94043

AUGUST 1998

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AIRBASE & ENVIRONMENTAL TECHNOLOGY DIVISION
TYNDALL AFB FL 32403-5323

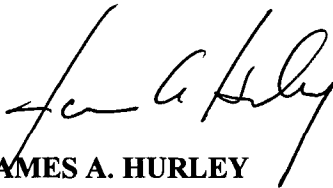
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JAMES A. HURLEY
Program Manager



CHRISTINE. WAGENER-HULME, Lt Col, USAF, BSC
Chief, Environmental Technology Development Branch



ANDREW D. POULIS
Scientific & Technical
Information Program Manager



NEIL J. LAMB, Col, USAF, BSC
Chief, Airbase & Environmental Technology Division

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Battelle 505 King Avenue Columbus Ohio 43201-2693 ARCADIS Geraghty & Miller, Inc. 555 Clyde Avenue Mountain View, CA 94043			8. PERFORMING ORGANIZATION REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words) The Air Force Air Logistics Centers (AF-ALCs) generate large quantities of sludges from their industrial waste water treatment plants (IWTPs). While these sludges are not toxic based on toxicity characteristic leachant procedure (TCLP) values, these are still classified as "F-waste" (e.g., F002, F005, F006) since the waste waters originate in plating and other metal finishing operations. The objective of this project was to identify and evaluate technologies to minimize the volume of these sludges. This report covers the final three tasks in the first phase of a 2-phase project: (a) site selection (Task 1.3), (b) sludge characterization (Task 1.4) and (c) laboratory testing (Task 1.5). The IWTP metal hydroxide sludges were characterized as predominantly organic (oil/grease, waste activated sludge, and hydrocarbons) at OL-ALC, inorganic at WR-ALC, and oily at OO-ALC. The sludges from IWTPs at OC-ALC and WR-ALC are conditioned with inorganic additives to make them dewaterable and as such the additives (predominantly iron and calcium compounds) comprise more than 50 percent of the treated sludge solids. The composition and quantities of the various IWTP sludges impacted the selection of technologies to minimize sludge volume disposed. The laboratory tests focused on (a) replacement of inorganic additives with polymers to achieve satisfactory dewatering, (b) cost-effective methods for drying, (c) alternative methods for metals removal from IWTP influent to minimize metallic sludge formation, and (d) on methods to reduce volume of biosludge to be disposed. Following successful laboratory				
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13. Abstract (Continued)

investigations in all four technology areas, brief field trials of polymer flocculation (at WR-ALC) and a drying technology (at OO-ALC) were carried out, which validated the laboratory results. The preferred technologies are recommended for Phase II field testing at various AF-ALCs.

PREFACE

This report represents the results of work done by Battelle in Columbus, Ohio, and ARCADIS Geraghty & Miller in Mountain View, California on the Phase I activities for "Treatment/Recycle of Contaminated Sludges", Contract No. F08637-95-D6003, Delivery Order 5300, with the Air Force Research Laboratory, Tyndall AFB, Florida.

The report covers the period of performance from June, 1995, to August, 1996, focusing on the characterization of selected AF-ALC sites and their IWTP sludges and the laboratory testing of technologies to minimize the amount of sludge to be disposed off site. Our team's efforts were enhanced through support of others. We would like to express our appreciation to Dan Luten and Freddie Hall of OC-ALC, Shawn Politino and Ellen Griffith of WR-ALC, Pat Sullivan of OO-ALC, Greg Valerie of SA-ALC, and Craig Burnett of SM-ALC for their assistance.

EXECUTIVE SUMMARY

A. BACKGROUND

The Air Force Air Logistics Centers (AF-ALCs) generate large amounts (300,000 to 1,000,000 gallons/day) of industrial waste waters that must be treated on-site to reduce the toxic (RCRA) metals, total suspended solids (TSS), fat, oil, and grease (FOG), and other toxic organic contaminants contributing to biological oxygen demand (BOD) and chemical oxygen demand (COD). The presence of solvent- and metal-bearing effluents from plating and metal-finishing shops leads to the formation of large quantities of "F-waste" (e.g., F002, F005, F006) in this waste water. As such, these sludges are classified as hazardous wastes and are, therefore, expensive to dispose.

In general, the AF-ALCs produce three basic types of industrial waste water treatment plant (IWTP) sludges: (a) metal hydroxide sludge; (b) biotreatment sludge (biosludge); and (c) oily sludge. However, often these sludges are mixed together and disposed as a combined sludge.

B. OBJECTIVE

The objectives of this project were to:

- Identify and characterize the problematic IWTP sludges at various AF-ALCs.
- Identify current and potential technologies for resource recovery, volume reduction, and/or detoxification of these IWTP sludges.
- Evaluate suitable technologies through laboratory and pilot-scale testing at an AF-ALC.
- Recommend technology prototyping and implementation.

A two-phase approach was used to meet the above objectives. This report documents the Phase I efforts to characterize ALC waste streams and perform laboratory testing.

C. APPROACH

The two-phased approach established seven tasks in Phase I to identify the sludge treatment/recycle needs at AF-ALCs and to evaluate and test candidate technologies at a

laboratory scale. These tasks are described in this report and establish the basis for proceeding to Phase II for pilot scale testing at the AF-ALCs.

Available data were collected from each of the five AF-ALCs to establish the quantity, composition, associated disposal cost and source of the IWTP sludges and were reported earlier⁽¹⁾. Additional samples were collected and analyzed to characterize the sludges from three AF-ALCs: OC-ALC; WR-ALC; and, OO-ALC. A literature review and technology selection effort identified potential technologies for each need⁽¹⁾. The technologies were ranked using a multiple attribute analysis based on technical and economic criteria. The preferred technologies were tested in the laboratory to determine the potential for waste reduction and associated cost savings. The data from these tests were used to match the recommended technologies to specific sites for pilot testing during Phase II.

D. SUMMARY OF KEY FINDINGS

1. AF-ALC IWTP Needs

The project team visited all five AF-ALCs to identify sludge disposal related needs at IWTPs. Based on AF-ALC inputs, each IWTP was analyzed in terms of (a) key IWTP unit operations, (b) major industrial operations contributing waste waters to the IWTP, (c) the chemical/additives usage within the IWTP, (d) effluent quantities and characteristics, (e) sludge disposal costs, (f) federal and local regulations impacting IWTP operations, (g) ongoing and planned IWTP upgrades, and (h) past, ongoing and planned technical efforts to address the sludge disposal problem.

Table 1 shows that three primary types of sludges, all of which are F-listed waste, are produced: (a) metal hydroxide sludge; (b) biosludge; and, (c) oily sludge. The oily sludge problem is unique to OC-ALC, which is currently addressing it under another project; therefore, it was excluded from this project. The AF-ALCs do not attempt to dispose the metal hydroxide sludge and biosludge separately; they merely combine the two before the final dewatering step. Collectively, the five AF-ALCs spend about \$1,240,000 per year to dispose the mixed sludges, with OC-ALC spending the most.

TABLE 1. SUMMARY OF IWTP SLUDGE CHARACTERISTICS AT AF-ALCs.

IWTP Sludge Characteristic	OC-ALC	WR-ALC	OO-ALC	SM-ALC	SA-ALC
Annual Sludge Disposal (tons/year) ^(a)	1440 (wet sludge) ----- 160 (dry sludge)	584 ^(b)	135	186	300
Type of Sludge	40% Metal hydroxide, 33% biosludge, and 27% oil and organics	90% metal hydroxide	Significant amount of oil and grease, 20% chrome	Mixture of biosludge, perlite and metal hydroxide sludge	Mixture of biosludge and calcium sulfate
Sludge Composition	9% solids; 91% water for wet sludge ----- 69% solids; 31% water for dry sludge	31% solids 69% water	56% solids 44% water	35% solids 65% water	35% solids 65% water
Unit Disposal Cost	\$0.18/lb for wet sludge; \$0.14/lb for dry sludge	\$0.22/lb	\$0.26/lb	\$0.51/lb	\$0.175/lb
Annual Disposal Cost	\$563,200	\$ 308,000	\$70,200	\$189,720	\$105,000
Chemistry Used for Metal Precipitation	FeSO ₄ /NaOH followed by FeS polishing	FeSO ₄ /NaOH	H ₂ SO ₄ /SO ₂ and NaOH	H ₂ SO ₄ /SO ₂ and NaOH	H ₂ SO ₄ /SO ₂ and NaOH with FeS for polishing

^(a) Excludes disposal of oily sludge.

^(b) Due to inefficient operation of the old filter press the current disposal rate is 5800 tons/year, but will be returned to previous levels once the press is replaced.

To supplement minimal amounts of available IWTP sludge data, the Acurex-Battelle Team (ABT) used its expert judgments and inputs from AF-ALC staff to identify opportunities (needs) for sludge quantity reduction. The following needs were identified:

- (1) Enhanced (mechanical) dewatering without using bulky additives. A related need is for cost-effective, environmentally-compliant drying after reaching a practical limit for mechanical dewatering.
- (2) Removal of toxic metals and excessive total suspended solids (TSS) from IWTP influents while minimizing the mass of precipitated matter, e.g., by use of alternative precipitation chemistry.
- (3) Biosludge volume reduction.
- (4) Resource recovery from (beneficial reuse of) sludge.

The ability to dewater sludges without using massive volumes of dewatering agents is the largest sludge need and provides the largest potential for reducing sludge disposal costs. After reaching the practical limits for mechanical dewatering, thermal drying can still be economical for further reducing the volume of sludge. This approach has the advantage of not altering the current IWTP operations. Furthermore, enhanced dewatering and efficient drying are important even if sludge minimization and/or resource recovery options are pursued.

The opportunities for reducing the mass of suspended solids formed during toxic metal precipitation and biodegradation of organic pollutants are primary targets for demonstration since that directly impacts the volume (cost) of sludge disposed even without enhanced dewatering and drying. However, this approach requires a much more careful examination of the compatibility with existing operations.

The resource recovery from the sludge may be a final step after the sludge-volume reduction options have been implemented.

2. Selection of Candidate Technologies

To address the general and specific AF-ALC needs, the project team identified candidate technologies based on (a) computerized literature search, (b) review of team's in-house

files, (c) vendor/industry surveys, and (d) inputs from Environics and AF-ALCs. The more pertinent technologies were then analyzed by project staff to allow a comparative evaluation. The technologies were then ranked using a multiple-attribute analysis with the following criteria, listed in order of importance:

- (1) Effectiveness in reducing sludge volume or disposal cost
- (2) Compatibility with existing operations
- (3) Rough-order-of-magnitude (ROM) cost
- (4) Feasibility of resource (e.g., water or mineral matter) reuse
- (5) Flexibility to adapt to future changes in overhaul and maintenance processes
- (6) Technology maturity.

TABLE 3. PRIORITIZED LIST OF AF-ALC SITES AND TOP RANKING TECHNOLOGIES FOR VARIOUS IWTP SLUDGE DISPOSAL NEEDS.

Need/Opportunity	AF-ALCs Impacted	Potential Technologies
(A) Dewatering/Drying	OC-ALC WR-ALC SA-ALC OO-ALC SM-ALC	(A-1) Flocculation/Dewatering (A-2) Alternative filter aids for Dewatering (A-3) Drying after Dewatering
(B) Metal Separation	WR-ALC OC-ALC OO-ALC SA-ALC	(B-1) Alternative Chemistry for metal precipitation (B-2) Membrane separation of Cr ^{VI} and metals (B-3) Liquid Ion Exchange Separation of Cr ^{VI} and metals
(C) Biosludge Minimization	OC-ALC SA-ALC WR-ALC	(C-1) Acid hydrolysis (C-2) Wet air oxidation (C-3) TEES
(D) Resource Recovery	OC-ALC WR-ALC OO-ALC SA-ALC SM-ALC	(D-1) Alternative Chemistry (D-2) Vittrification with beneficial reuse

The top ranking technologies to address the four specific needs are listed in Table 3. The use of polymeric flocculants was identified as a key technology to enhance dewatering. The use of more effective, less-costly filter aids was also identified as a second option. These are the lowest capital cost options as all AF-ALCs currently own filter presses and the capital cost for flocculation and addition of filter aids is minimal.

A number of drying technologies, including spray drying, fluid bed drying, flash drying, and low-humidity air drying, were identified. All of these options involve significant capital outlays, but can still have quick payback. The preferred technology needs to be an improvement over the current drying technology employed by AF-ALCs with respect to reliability of operations and air emissions.

Several alternative chemistry methods were identified with the potential to reduce the concentration of Cr^{VI} and RCRA metals (e.g., Cd and Cr^{III} , in the waste water without requiring the addition of large quantities of chemicals to reduce Cr^{VI} and precipitate the RCRA metals. Additionally, liquid ion exchange (LIX) and membrane separation were identified for removal of various undesirable ions from water. All of these methods will significantly alter the IWTP operations but may also produce a concentrated waste that could be recycled to metal recovery.

Biosludge is currently produced at OC-ALC and SA-ALC and future modifications at other AF-ALCs may produce a similar biosludge. The biosludge is generally very difficult to dewater without extensive use of chemical pretreatment and bulking agents. Therefore, technologies to partially or fully convert the biosolids to gas (CH_4 , CO_2 , H_2O) were identified. Some of these technologies have been known for quite some time but none have been adequately evaluated for addressing the AF-ALC needs. All of these technologies involve significant capital outlays but appear to be economically viable. The economic viability is expected to increase if the technology focus is on maximizing filterability through thermal conditioning.

Resource recovery to utilize final sludge solids was not recommended for testing unless the other technology options failed. Besides, a couple of the AF-ALCs are separately evaluating these options.

3. Site Selection and Sludge Characterization

For the various technologies selected for evaluation, the range of sludge volume reduction was estimated and thus the AF-ALC sites with the highest potential for saving in sludge cost disposal were identified (see Table 3). These sites were subjects of additional IWTP and sludge characterization. The focus for target technologies was as follows: (a) flocculation/dewatering -- WR-ALC and OC-ALC; (b) drying -- OC-ALC and OO-ALC; (c) Cr^{VI} reduction and metal separation -- WR-ALC and OC-ALC; and (d) biosludge reduction -- OC-ALC. This effort led to (a) an understanding of the sludge production and characteristics as a function of the specific IWTP design and operation, (b) a characterization of sludges that helped define laboratory tests, and (c) selection of samples at specific locations for laboratory testing.

The analyses of the sludges at the three AF-ALCs show similarity in the composition of the metal hydroxide sludges, particularly the presence of iron compounds in large quantities at OC-ALC and WR-ALC. Iron is added to the IWTP streams in order to reduce Cr^{VI} to Cr^{III} and coagulate fine particles from RCRA metal precipitation. The iron compounds constitute about 90 percent of the suspended solids content of the untreated metal hydroxide sludges at OC-ALC and at WR-ALC. The RCRA metals that are removed from the waste water by these processes are only a small portion (less than about 10 percent) of the total metal hydroxide sludge solids.

Biosludge is present only in the OC-ALC IWTP; however, the upgrade of the IWTP at WR-ALC to include a biotreatment process will produce about 12 tons/month of biosludge based on the BOD/COD analysis.

Lime is added in the sludge treatment at WR-ALC and OC-ALC to enhance dewatering. The resulting waste for disposal consists of 60 to 95 percent additives, on a sludge solids basis, introduced during waste water treatment at the IWTP. Therefore, a key target for reducing sludge volume is elimination/reduction of additives (iron and calcium compounds) through use of alternative technologies for waste water treatment.

4. Laboratory Testing

All technologies tested -- flocculation/dewatering, advanced drying, alternate Cr^{VI}

reduction and metal removal, and biosludge reduction -- were shown to be technically feasible in significantly reducing the volume of the target sludge. A summary of capital and operating costs and simple payback periods are summarized in Table 51. All technologies except two indicate an economic potential with payback periods ranging from about 0.2 to about 3 years. An important point to be noted is that these technologies cannot be rank ordered in terms of payback alone as they apply to different types (composition and consistency) of sludges. The net volume reduction for all IWTP sludges from a given AF-ALC as well as capital investment must also be considered. Another key point is that all technologies tested have an existing commercial basis although the application in the past to AF-ALC needs has generally been absent.

a. Flocculation/Dewatering

Pressure filtration (dewatering) may be combined with flocculation, the use of a precoat and different treatment strategies to dewater sludges at OC-ALC and WR-ALC. The strategy identified for the cost effective application of pressure sludge dewatering at OC-ALC is the separation of the two waste streams; IWTP #10 (biosludge) and IWTP #8 (metal hydroxide sludge). The biosludge may be treated by addition of ferric chloride and lime followed by gravity thickening and pressure filtration. It was demonstrated that the metal hydroxide sludge (IWTP #8) could be thickened and then treated with a flocculant (e.g., Cyttec 837 or Calgon Pol-E-Z-692) followed by pressure filtration with a precoated filter. The disposal and treatment cost savings, that may be achieved if the dryer installed at OC-ALC is used, were estimated to be \$450,300 per year and the capital expenditure is estimated to be about \$222,700. Payback is, therefore, expected to be 6 months.

Treatment of WR-ALC metal hydroxide sludge IWTP #17 by flocculation (e.g., Percol 727 or Cyttec 1820) followed by pressure filtration (without precoat) was successfully demonstrated in the laboratory as well as at the WR-ALC IWTP. Based on the field tests (reported elsewhere), the estimated savings are \$31,700 per year and the capital cost to install a polymer mixing system was estimated to be \$64,000. Thus, the payback is estimated to be 2 years.

TABLE 51. COST SUMMARY FOR ALTERNATIVE IWTP PROCESSES PROPOSED.

AF-ALC Site/Plant	Technology	Sludge Quantity Eliminated		Baseline Waste Disposal Cost (\$/yr)	Net Annual Savings (\$)	Installed Capital Cost (\$)	Simple Payback (years)
		tons/yr	Weight Reduction (%)				
Flocculation/Dewatering							
WR-ALC IWTP #17	Polymer Flocculation	92	16	257,000	31,700	64,400	2.0
OC-ALC IWTP #8 and #10	Polymer Flocculation	1,209	75	617,800	450,300	222,700	0.5
Drying							
OO-ALC	Low humidity drying	41	32	163,300	120,000	116,200	1.0
WR-ALC	Low humidity drying	358	61	257,000	108,200	348,500	3.2
Metal Reduction							
WR-ALC IWTP Plant #1 and #2	Reduced FeSO ₄ use and improved Sludge Blanket	438	75	257,000	176,700	32,900	0.2
WR-ALC IWTP Plant #2	Reduced FeSO ₄ use and Mixing/Oil Skimming (MOS) LLX	370	63	257,000	140,500	84,000	0.6
WR-ALC IWTP Plant #2	Chrome A-LIX	273	47	257,000	101,200	84,000	0.8
WR-ALC IWTP Plant #2	Chrome A-LIX and MOS LLX	380	65	257,000	126,800	168,000	1.3
OC-ALC	Reduced FeSO ₄ use and improved Sludge Blanket	344	22	617,800	60,900	48,900	0.8
OC-ALC Stream D3	Chrome A-LIX	73	5	617,800	7,200	84,000	11.6
OC-ALC Stream D3	Reduced FeSO ₄ use and MOS-LLX	212	13	617,800	57,200	84,000	1.5
OC-ALC Stream D3	Chrome A-LIX and MOS LLX	215	13	617,800	39,100	168,000	4.3

b. Drying

Four different drying technologies -- low-humidity drying, flash drying, spray drying, and pulse-combustion drying -- were evaluated after screening the options from a longer list of commercially-available technologies. A pilot test of the JWI low-humidity dryer was conducted at Tooele Army Depot using dewatered (pressed) sludges from OO-ALC. A batch of 1430 pounds was dried over a 2-day test period. The solids content was increased from 36.0 to 60.6 percent. The operation was simple and labor to operate it is estimated to be minimal. A payback of 1 year was estimated. The results from the other drying tests are reported separately.

c. Metal Reduction/Removal

Four technologies for testing alternate methods to remove Cr^{VI} and RCRA metals (specially Cd, Cr^{III} , Cu, and Pb) were tested: (a) mixing/oil skimming (MOS), which is a form of liquid-liquid extraction (LLX) used for metal separation; (b) anion liquid ion exchange (A-LIX) used to extract Cr^{VI} ; (c) optimized precipitation using impurity metal precipitate as a sludge blanket; and (d) minimization of ferrous sulfate (FeSO_4) use to reduce Cr^{VI} . From the successful laboratory testing using simulated IWTP waste water as well as actual OC-ALC waste water, the following treatment options were developed:

- (i) Use a stoichiometric amount of FeSO_4 to reduce Cr^{VI} and build an SCC blanket of sludge out of the impurities without adding excessive amounts of FeSO_4 as is practiced now to form a blanket.
- (ii) Use only a stoichiometric amount (rather than about 20 times the stoichiometric amount used at present) of FeSO_4 to reduce Cr^{VI} followed by MOS LLX for broad spectrum metal removal.
- (iii) Extract Cr^{VI} by A-LIX for potential process recycle of hexavalent chrome, followed by MOS LLX for broad spectrum metal removal of diluted waste water just before the solids contact clarifier (SCC).

The first two options have payback of 1.5 years or less.

All three metal separation options as well as the use of A-LIX alone were found to be economical options for WR-ALC as shown in Table 51.

d. Biosludge Reduction

Three technologies -- acid hydrolysis, wet air oxidation, and TEES -- were experimentally evaluated. The first two of these technologies were recommended for bench-scale studies under a follow-on project funded by OC-ALC. Of these, the acid hydrolysis system has a better payback (1.6 years), but wet air oxidation is commercially proven.

E. RECOMMENDATIONS FOR PHASE II

The following technologies are proposed for field demonstration at various AF-ALCs based on potential for sludge volume reduction and payback criteria. Additional rationale for testing are provided below:

(1) Flocculation/Dewatering

Since dewatering is the largest single need and since enhanced dewatering has a positive impact even if source reduction reduces the amount of suspended metal hydroxide and biosludge solids it is given the highest priority for testing. The two demonstrations proposed are:

- (1A) WR-ALC --** The WR-ALC IWTP produces a large amount of metal hydroxide sludge using an excessive amount of lime. The use of polymers can potentially eliminate the use of lime. The proposed field test data can be used immediately by WR-ALC to implement the process as they are in the midst of an IWTP upgrade.
- (1B) OC-ALC --** The OC-ALC IWTP produces more sludge than WR-ALC, but the OC-ALC sludge is different in its dewatering behavior because of the presence of biosludge. The proposed scheme to dewater this sludge is to use polymers to flocculate the metal hydroxide sludge and use the conventional ferric chloride and lime conditioning for biosludge and then dewater these two treated sludges. This scheme will serve as a benchmark for the thermal conditioning/treatment technology selected in Item 4 below. The results on dewatering of the mixed sludge will be pertinent for future operations at WR-ALC when they install a biotreatment facility.

(2) Metal Separation

The OC-ALC, WR-ALC, and SA-ALC IWTPs use large amounts of iron compounds to reduce Cr^{VI} and RCRA metals. It is proposed that two alternate technologies be tested at OC-ALC or WR-ALC to reduce the amount of iron compounds used and thus achieve source reduction. The two technologies proposed can not only benefit the Air Force, but also other DoD and industrial facilities.

- (2A) The use of mixing/oil skimming (MOS) technology to remove RCRA metals in conjunction with use of a theoretical amount of FeSO_4 to reduce Cr^{VI} is proposed. A pilot plant for the MOS, a liquid-liquid extraction technique, is already available from a previous Environics project. A benchmark for evaluating this technology should be the use an SCC sludge blanket made out of the impurities in the feed waste water.
- (2B) After successful demonstration of 2A, the metal separation technology can be further advanced by replacing FeSO_4 treatment with liquid ion exchange to remove Cr^{VI} . The MOS pilot plant can be modified for this additional testing.

(3) Drying

While thermal drying can be a cost effective means to further reduce the cost of sludge disposal, its impact is expected to be less than through enhanced dewatering and source reduction through alternate methods to remove metals. However, drying can be a higher priority if dewatering and source reduction are unsuccessful or if the currently used drying systems need to be improved as in the case proposed below.

- (3A) OO-ALC -- The dewatered sludge at OO-ALC is quite oily and causes undesirable air emissions from the current dryer. The emissions can be eliminated with low-humidity drying (a JWI system). The Phase I pilot tests were successful and the data were used by OO-ALC to specify a full-scale system. It is recommended that the full-scale system performance be documented and economics re-evaluated based on testing at OO-ALC.

This drying system could be the system of choice for future IWTP upgrades at OC-ALC and WR-ALC.

(4) Biosludge Reduction

Biosludge dewatering is a major problem for a large number of IWTPs across various industries and for municipalities. It is a major problem for OC-ALC and a current problem at SA-ALC. Also, WR-ALC is likely to encounter this problem in the near future. Therefore, treatment of biosludge to alter its dewatering behavior and its suspended solids content is recommended based on Phase I results. However, a separate program already funded by OC-ALC is the proposed program for demonstrating the preferred technologies, i.e., acid hydrolysis and wet air oxidation/thermal conditioning.

In recommending the above technologies, a number of other technologies were eliminated from consideration. Examples of the technologies not recommended are: (1) polymer flocculation of mixed sludge at OC-ALC; (2) use of A-LIX for removal of Cr^{VI} alone at OC-ALC; (3) conventional drying technologies that cause potential air emission problems such as fluid bed and flash dryers.

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ABBREVIATIONS, ACRONYMS AND SYMBOLS

AF-ALC	Air Force-Air Logistic Centers
ASTM	American Society for Testing of Materials
APHA	American Public Health Association
A-LIX	Anion-LIX
atm	atmosphere
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
Cr^{III} , Cr^{3+}	Chromium with charge of 3+; also Chromium(III)
Cr^{VI} , Cr^{6+}	Chromium with charge of 6+; also Chromium(VI)
DRMO	Defense Reutilization and Marketing Office
E/A or V_E/V_{aq}	Organic solvent (or extractant phase) to aqueous phase volume ratio
E_M	Percent extraction of metal M
EM	Environmental Management
EPA	Environmental Protection Agency
FOG	Fat, Oil and Grease
gpd	gallons per day
ICP or ICAP	Inductively coupled Argon Plasma Elemental Analysis Technique
IWTP	Industrial Waste Water Treatment Plant
LIX	Liquid Ion Exchange
$[M]_A$	Concentration of metal M in aqueous phase
$[M]_E$	Concentration of metal M in extractant phase
MOS	Mixing/Oil Skimming
M-T	McCabe-Thiele Plot
MOS-LLX	Mixing/Oil Skimming Liquid Liquid Extraction
NPDES	National Pollutant Discharge Elimination System
OC-ALC	Oklahoma City Air Logistics Center
OO-ALC	Ogden Air Logistics Center
overbar	Chemical species dissolved in extractant phase (LIX), e.g.,
q	Distribution coefficient in LIX processing,
RCRA	Resource Conservation and Recovery Act
SA-ALC	San Antonio Air Logistics Center
SCC	Solids Contact Clarifier
SM-ALC	Sacramento Air Logistics Center
TCLP	Toxicity Characteristic Leachant Procedure
TAD	Tooele Army Depot
TDS	Total Dissolved Solids
TEES®	Thermal Environmental Energy System
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VOC	Volatile Organic Carbon
WAO	Wet Air Oxidation
WR-ALC	Warner Robins Air Logistics Center

SECTION I

INTRODUCTION

The U.S. Air Force seeks solutions to reduce or eliminate the large volumes of sludges that are produced at industrial waste water treatment plants (IWTP). The sludges can contain varying quantities of hazardous materials, such as heavy metals, waste oils, and halogenated organic compounds, in a matrix of solids and water. These sludges are currently disposed as hazardous waste. Increasingly stringent environmental legislation and rising disposal costs require that these streams be reduced or eliminated. As an initial step to meet this requirement, technology to minimize the volume and/or the toxicity of these sludges need to be identified and evaluated.

A. OBJECTIVES

The project objectives were to:

- Identify and characterize the problematic IWTP sludges at the AF-ALCs
- Identify current and potential technologies for resource recovery, volume reduction and/or detoxification of these IWTP sludges
- Qualify, through laboratory testing, suitable technologies to be validated at bench or small pilot-scale at an AF-ALC
- Recommend technology prototyping and implementation.

A two-phased approach was planned to meet the above objectives. This report documents the Phase I actions to identify and evaluate site specific needs and candidate technologies. Preferred technologies were experimentally tested using sludges obtained from AF-ALC sites. During Phase II, pilot-scale tests at an AF-ALC will evaluate the most preferred technology(s) selected in Phase I.

B. BACKGROUND

The AF-ALCs generate large amounts (300,000 to 1,000,000 gallons per day) of industrial waste water that must be treated on-site to reduce the toxic (RCRA) metals; total

contributing to BOD and COD. This treatment leads to the formation of large quantities of "F-waste" (e.g., F002, F005, F006) due to the presence of solvent and metal bearing effluents from plating and metal finishing operations. Such wastes are classified as hazardous because of the "derived from" regulations and therefore carry expensive disposal costs.

In general the AF-ALC's produce three types of IWTP sludges: metal hydroxide sludge, biotreatment sludge and oily sludge. Each sludge has some organic content (BOD/COD) and total suspended solids (TSS) with water still the dominant constituent. These sludges are sometimes mixed for disposal. The needs survey (Task 1.1) and sludge characterization tasks (Task 1.4), described below, quantified each sludge and the composition range for each AF-ALC.

C. APPROACH

The two-phased approach established seven tasks in Phase I to identify the sludge treatment/recycle needs at AF-ALCs and to evaluate and test candidate technologies on a laboratory scale. These tasks are described in this report and establish the basis for proceeding to Phase II for pilot scale testing at the AF-ALCs. Figure 1 presents the Work Breakdown Structure for the project as an overview of the major work elements.

Available data were collected from each of the five AF-ALCs to establish the quantity, composition, associated disposal cost and source of the IWTP sludges. Additional samples were collected and analyzed to characterize the sludges. A literature review and technology selection effort identified potential technologies for each need. The technologies were ranked using a multiple attribute analysis based on technical and economic criteria. Laboratory testing established the potential waste reduction and cost savings that could be achieved with the candidate technologies and sludge streams. These tests were used to further establish the recommended technologies and sites for pilot testing during Phase II.

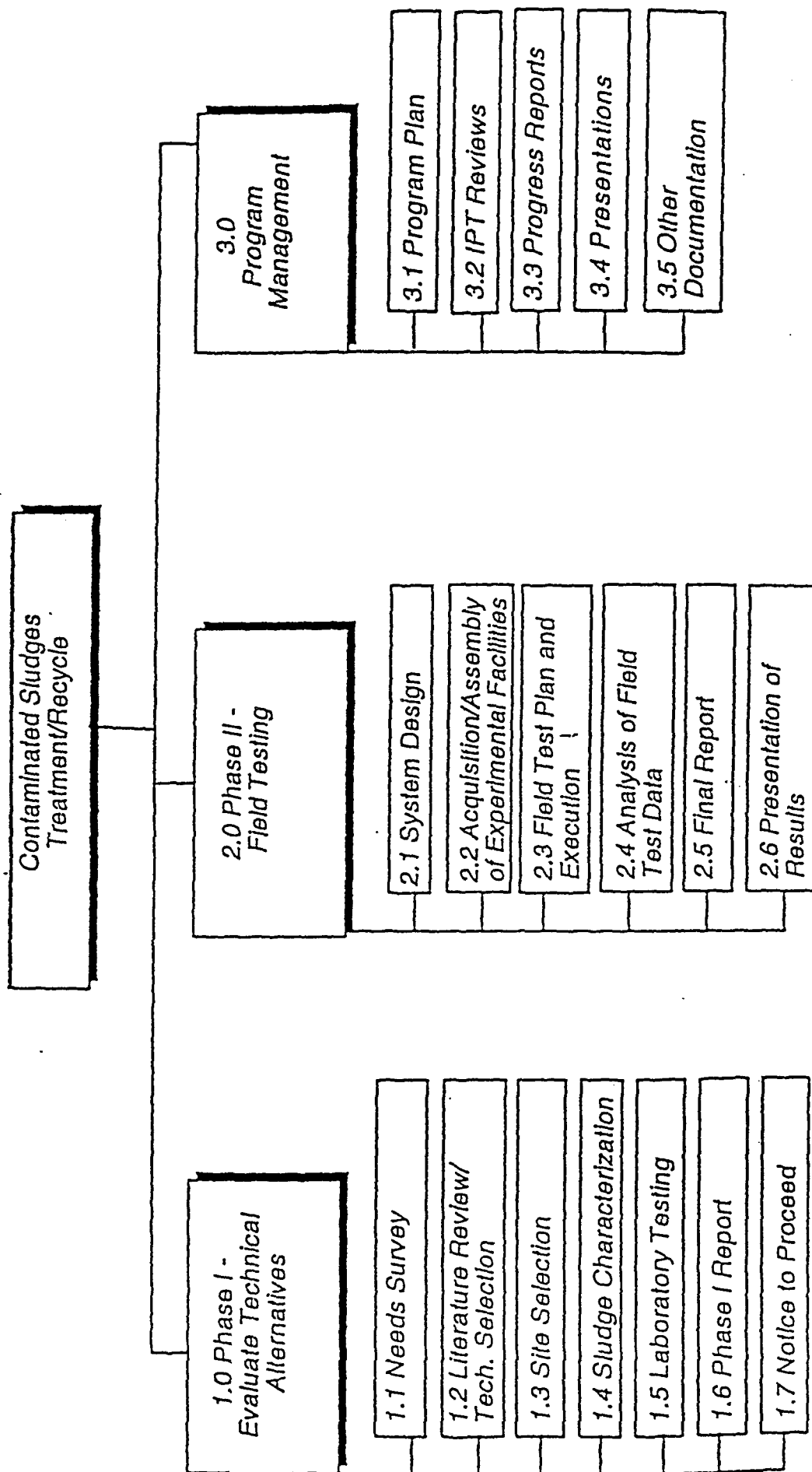


Figure 1. Contaminated Sludge Treatment/Recycle Project Work Breakdown Structure.

SECTION II

NEEDS SURVEY

The complete Needs Survey (Task 1.1) was documented in a Technical Report⁽¹⁾ submitted on November 21, 1995. The following summary presents the updated needs for each AF-ALC from that report.

The project team visited all five AF-ALCs to identify sludge disposal related needs at IWTPs. The primary contacts were pollution prevention and compliance staff in Environmental Management (EM) knowledgeable about IWTP operations, DRMO people responsible for keeping sludge disposal records, and IWTP foreman and operators. Based on these inputs, each AF-ALC IWTP was analyzed in terms of (a) key IWTP unit operations, (b) major industrial operations contributing waste waters to IWTP, (c) the chemical/additives usage within the IWTP, (d) effluent quantities and characteristics, (e) sludge disposal costs, (f) federal and local regulations impacting IWTP operations, (g) ongoing and planned IWTP upgrades, and (h) past, ongoing and planned technical efforts to address the sludge disposal problem.

Information was obtained on sludge disposal quantities, costs and toxicity characteristic leachant procedure (TCLP) values for all AF-ALCs. Basically, all TCLP values were within allowable limits with respect to metals and toxic organics. While this would make the sludges nonhazardous, they are still disposed as F-listed hazardous waste because of the origin of the influents to IWTPs (i.e., derived from metal plating operations). None of the AF-ALCs plan to "delist" the sludges because of the time consuming procedures for delisting. The problem is not one of detoxifying the sludges, but of reducing the quantity and, therefore, the sludge disposal costs. This required a detailed analysis of the various unit operations and their respective sludges.

Table 1 shows that three primary types of sludges, all of which are F-listed waste, are produced: (a) metal hydroxide sludge, (b) biosludge, and (c) oily sludge. The oily sludge problem is unique to OC-ALC, which is currently addressing it under another project; therefore, it was excluded from this project. The AF-ALC's do not attempt to dispose the metal hydroxide sludge and biosludge separately; they merely combine the two before the final dewatering step. Collectively, the five AF-ALC's spend about \$1,240,000 per year to dispose the mixed sludges, with OC-ALC spending the most.

TABLE 1. SUMMARY OF IWTP SLUDGE CHARACTERISTICS AT AF-ALCs.

IWTP Sludge Characteristic	OC-ALC	WR-ALC	OO-ALC	SM-ALC	SA-ALC
Annual Sludge Disposal (tons/year) ^(a)	1440 (wet sludge) ----- 160 (dry sludge)	584 ^(b)	135	186	300
Type of Sludge	40% Metal hydroxide, 33% biosludge, and 27% oil and organics	90% metal hydroxide	Significant amount of oil and grease, 20% chrome	Mixture of biosludge, perlite and metal hydroxide sludge	Mixture of biosludge and calcium sulfate
Sludge Composition	9% solids; 91% water for wet sludge ----- 69% solids; 31% water for dry sludge	31% solids 69% water	56% solids 44% water	35% solids 65% water	35% solids 65% water
Unit Disposal Cost	\$0.18/lb for wet sludge; \$0.14/lb for dry sludge	\$0.22/lb	\$0.26/lb	\$0.51/lb	\$0.175/lb
Annual Disposal Cost	\$563,200	\$ 308,000	\$70,200	\$189,720	\$105,000
Chemistry Used for Metal Precipitation	FeSO ₄ /NaOH followed by FeS polishing	FeSO ₄ /NaOH	H ₂ SO ₄ /SO ₂ and NaOH	H ₂ SO ₄ /SO ₂ and NaOH	H ₂ SO ₄ /SO ₂ and NaOH with FeS for polishing

^(a) Excludes disposal of oily sludge.

^(b) Due to inefficient operation of the old filter press the current disposal rate is 5800 tons/year, but will be returned to previous levels once the press is replaced.

The project team used both its expert judgement and ALC staff input to supplement the minimal amount of data available on the various ALC IWTP intermediate sludge stream. From this information ABT identified the following opportunities (needs) for sludge reduction:

- (1) Enhanced (mechanical) dewatering without using bulky additives. A related need is for cost-effective, environmentally-compliant drying after reaching a practical limit for mechanical dewatering.
- (2) Removal of toxic metals and excessive total suspended solids (TSS) from IWTP influents while minimizing the mass of precipitated matter, e.g., by use of alternative precipitation chemistry.
- (3) Biosludge volume reduction.
- (4) Resource recovery from (beneficial reuse of) sludge.

The potential economic benefits from achieving the first three objectives were estimated as shown in Table 2. A fourth opportunity/need relates to resource recovery from the final sludge produced after implementing technologies to address the above three needs.

The ability to dewater sludges without using massive volumes of dewatering agents is the largest sludge need and provides the largest potential for reducing sludge disposal costs. After reaching the practical limits for mechanical dewatering, thermal drying can still be economical for further reducing the volume of sludge. This approach has the advantage of not altering the current IWTP operations. Furthermore, enhanced dewatering and efficient drying are important even if sludge minimization and/or resource recovery options are pursued.

The opportunities for reducing the mass of suspended solids formed during toxic metal precipitation and biodegradation of organic pollutants are primary targets for demonstration since that directly impacts the volume (cost) of sludge disposed even without enhanced dewatering and drying. However, this approach requires a much more careful examination of the compatibility with existing operations.

The resource recovery from the sludge may be a final step after the sludge-volume reduction options have been implemented.

TABLE 2. SUMMARY OF OPPORTUNITIES FOR IWTTP SLUDGE
REDUCTION AND EXPECTED SAVINGS AT AF-ALCs.

Applicable Need	OC-ALC	WR-ALC	OO-ALC	SM-ALC	SA-ALC	Total for all ALCs
Additional Dewatering Applicability	Yes	Yes	Limited Applicability	Yes	Yes	
Annual Savings from Dewatering, (\$/yr)	469,900	131,000	10,000	94,900	52,500	758,300
Alternative to Ca(OH) ₂ Addition as Filter-Aid	Yes	Yes	No	No	Yes	
Annual Savings from Elimination of Ca(OH) ₂ , (\$/yr)	100,800	53,000	0	0	34,650	188,450
Alternative Chemistry for Metal Precipitation	Yes	Yes	Limited Applicability	No	Yes	
Annual Savings from Alternative Chemistry, (\$/yr)	180,000	246,000	17,550	0	26,300	469,850
Biosludge Destruction	Yes	No	Yes	Limited Applicability	Yes	
Annual Savings from Biosludge Destruction, (\$/yr)	216,000	0	28,100	30,400	42,000	316,500

SECTION III

TECHNOLOGY REVIEW

The complete Literature Review/Technology Selection (Task 1.2) was documented in the Technical Report⁽¹⁾ submitted on November 21, 1995. The following summary presents the priority technologies that are described in subsequent testing sections.

To address the general and specific AF-ALC needs, the project team identified candidate technologies based on (a) computerized literature search, (b) review of team's in-house files, (c) vendor/industry surveys, and (d) inputs from Environics and AF-ALCs. The more pertinent technologies were then analyzed by project staff to allow a comparative evaluation. The technologies were then ranked using a multiple-attribute analysis using the following criteria, listed in order of importance.

- (1) Effectiveness in reducing sludge volume or disposal cost reduction
- (2) Compatibility with existing operations
- (3) Rough-order-of-magnitude (ROM) cost
- (4) Feasibility of resource (e.g., water or mineral matter) reuse
- (5) Flexibility to adapt to future changes in overhaul and maintenance processes
- (6) Technology maturity.

The candidate technologies identified to address the four specific needs are listed in the Table 3.

TABLE 3. PRIORITIZED LIST OF AF-ALC SITES AND TOP RANKING TECHNOLOGIES FOR VARIOUS IWTP SLUDGE DISPOSAL NEEDS.

Need/Opportunity	AF-ALCs Impacted	Potential Technologies
(A) Dewatering	OC-ALC WR-ALC SA-ALC OO-ALC SM-ALC	(A-1) Flocculation/Dewatering (A-2) Alternative filter aids for Dewatering (A-3) Drying after Dewatering
(B) Metal Separation	WR-ALC OC-ALC OO-ALC SA-ALC	(B-1) Alternative Chemistry for metal precipitation (B-2) Membrane separation of Cr ^{VI} and metals (B-3) Liquid Ion Exchange Separation of Cr ^{VI} and metals
(C) Biosludge Minimization	OC-ALC SA-ALC WR-ALC	(C-1) Acid hydrolysis (C-2) Wet air oxidation (C-3) TEES
(D) Resource Recovery	OC-ALC WR-ALC OO-ALC SA-ALC SM-ALC	(D-1) Alternative Chemistry (D-2) Vittrification with beneficial reuse

A. DEWATERING/DRYING

Enhanced, mechanical dewatering of sludges was the largest single need from the AF-ALCs perspective and provides largest potential cost reduction. Improved dewatering aids (flocculants, filter aids, and precoat) offered potential reductions in sludge quantities and disposal costs. Up to half of the current sludge quantity is the result of chemicals added at the IWTP to improve and filter performance. Several flocculants were identified that could replace the lime currently being added prior to filtration. This has the potential to reduce the quantity of resulting sludge and the solids content of a filter cake. Also alternative filter aids and precoat were identified to improve filter performance.

Commercial dryers are available that produce more than 70 percent solids with improved reliability over the existing equipment currently used at some AF-ALCs. Low temperature dryers are of interest because VOC emissions are a potential concern. Capital and operating costs are critical to realizing net cost savings.

B. METAL SEPARATION

Several alternative chemistry methods were identified with the potential to reduce the concentration of Cr^{VI} and RCRA metals (e.g., Cd and Cr^{III}) in the waste water without requiring the addition of large quantities of chemicals to reduce and precipitate the dissolved metal contaminants. Additionally, liquid ion exchange (LIX) and membrane separation were identified for removal of various undesirable ions from water. All of these methods will significantly alter the IWTP operations but may also produce a concentrated waste that could be recycled for metal recovery. This approach is most attractive for concentrated influents to the IWTP such as the chrome sump at OC-ALC.

The primary technology identified for metals separation is LIX. It is used for separation and recovery of dissolved inorganic ions from water with commercial applications in the mining and metal purification industries. Use of an immiscible organic solvent, such as high flash point kerosene, and an organic extractant can concentrate and remove metal contaminants from the waste water without requiring the excessive addition of chemicals currently used at the IWTPs. The resulting metal concentrations in the effluent streams are expected to be below current NPDES discharge limits. The LIX can replace the current IWTP operations consisting of the reduction, coagulation and precipitation steps which produce excessive amounts of sludge.

C. BIOSLUDGE MINIMIZATION

Biosludge is currently produced at OC-ALC and SA-ALC and future modifications at other AF-ALCs may produce a similar biosludge. The biosludge is generally very difficult to dewater without extensive use of chemical pretreatment and bulking agents. Therefore, technologies to partially or fully convert the biosolids to gas (CH₄, CO₂, H₂O) were identified. Some of these technologies have been known for quite some time but none have been adequately evaluated for addressing the AF-ALC needs. All of these technologies involve significant capital outlays but appear to be economically viable. The economic viability is expected to increase if the technology focus is on maximizing filterability through thermal conditioning rather than on solubilizing or gasifying the biosolids. The two leading technologies identified were acid hydrolysis and wet air oxidation (WAO).

The WAO is a thermal chemical oxidation process that is carried out in an aqueous environment at elevated temperatures and pressures. It is used primarily to oxidize organic contaminants and other hazardous wastes. Compressed air is the usual source of oxygen. WAO systems are typically operated at 150 to 320 C and 20 to 200 atm (300 to 3000 psig). The relatively high capital and operating costs have limited the commercial applications for nonhazardous streams.

Acid hydrolysis is a developing technology that breaks organic contaminants into smaller molecules by hydrolysis reactions with water. The resulting products, carboxylic acids, are water soluble and can be recycled for additional destruction in the aeration treatment basin. The quantity of remaining solids are minimized and filter much easier than the original biosludge.

SECTION IV

SITE SELECTION AND SLUDGE CHARACTERIZATION

Task 1.1 of Phase I of the project was designed to gather information needed in site selection for field demonstration of sludge reduction technologies. The sludge volume reduction needs at each AF-ALC site were evaluated by collection and review of waste disposal data from the individual AF-ALCs. Site selection and analysis of the compositions of sludge streams and industrial waste water treatment plant (IWTP) process streams were performed as part of Tasks 1.3 and 1.4. The process stream compositions at OC-ALC had been previously determined as part of a project to reduce oily sludge volumes and to recycle oily process waste water⁽²⁾.

Site selection was guided by considering the volumes of each type of sludge produced at the sites and the preferred technologies selected for application to the different sludge types in the technology assessment. Laboratory testing was performed on the selected sludges to determine the technology applicability and the optimum operating conditions. This section covers the site selection (Task 1.3) and sludge characterization (Task 1.4).

A. SITE SELECTION

The needs of the AF-ALC's were prioritized based on the sludge disposal costs summarized in Table 1, and whether the IWTP discharges are in compliance with regulatory requirements. The survey of current practices of IWTPs at AF-ALCs indicates that sludge disposal volumes and costs can be reduced at each site. While there is some commonality in the needs and applicable technologies, the extent of sludge volume reduction and expected savings vary among the AF-ALCs. The estimated cost savings opportunities (Table 2) were based solely on reduction in sludge disposal volumes for each technology (such as additional dewatering) at each AF-ALC without consideration of changes in operating and amortized capital costs. The operating cost and capital cost estimates require data from laboratory and pilot tests planned for Tasks 1.5 and 2.3 of this project.

The sites with the highest potential for cost savings were chosen for additional analysis and laboratory experiments with the appropriate technologies. The following list summarizes the sites selected for evaluating the applicability of each technology.

- (1) WR-ALC and OC-ALC streams containing large quantities of lime were selected for enhanced dewatering and lime elimination studies. Polymeric flocculants combined with diatomaceous earth filter precoats aids are expected to have highest cost reduction potential on these streams.
- (2) OC-ALC and WR-ALC were chosen to evaluate alternative metal precipitation technologies that minimize the use of iron compounds.
- (3) OO-ALC and OC-ALC were selected for studying the application of advanced drying technologies that can handle oily sludges while meeting air emission standards.
- (4) OC-ALC was selected for testing methods to reduce mass of biosludge solids. The OC-ALC IWTP produces the largest amount of biosludge among the five AF-ALCs⁽³⁾.

These three sites, OC-ALC, WR-ALC, and OO-ALC were subject of detailed analyses of the processes used in their IWTPs and of the sludges produced. The results of these analyses are provided in this section.

B. GENERAL RESULTS OF IWTP STREAM CHARACTERIZATION

1. Sources of Contaminants in AF-ALC IWTP Streams

The aircraft maintenance/repair processes employed at AF-ALCs were analyzed to determine the sources of the contaminants in the streams entering the IWTPs at OC-ALC, WR-ALC and OO-ALC. Interviews with AF-ALC personnel provided the information used in this analysis. The aircraft maintenance operations of the AF-ALC's are similar. All AF-ALC sites provide cleaning and refurbishing services that introduce contaminants to the AF-ALC waste waters. Since ongoing projects for sludge treatment at OC-ALC involved some analysis of IWTP streams, OC-ALC was chosen as a model for waste generation at the AF-ALC's.

Paint removal from the exterior of aircraft, grease, dirt and soot removal from engine parts and corrosion treatment at the plating shop introduce the primary contamination into the AF-ALC waste water. This includes paint chips, chromium, metals, carbon from soot, grease from engines and phenol from paint stripping. Further waste is introduced from floor sweepings and rinse waters from the automotive workshops. Spent cleaner and degreaser solutions introduce significant organic waste into the IWTP influent. Cooling and scrubbing water from the engine test cells at OC-ALC also introduce solids, oil, and fuel.

IWTP operations at OC-ALC and WR-ALC introduce significant quantities of iron as ferrous sulfate during metal treatment and lime is added during the final treatment of the sludges prior to pressure filtration. These additives to the IWTP wastes are a large portion of the overall quantity of sludge produced by WR-ALC and OC-ALC. The metal precipitation at OO-ALC does not involve the addition of ferrous sulfate and, therefore, OO-ALC does not dispose large quantities of iron and lime in its sludges. Detailed analysis of the IWTP processes and the sludges is provided in parts C, D, and E in this section.

2. Analytical Techniques for IWTP Stream Characterization

The influent, intermediate, and effluent streams for the IWTPs were analyzed using standard tests to address the following objectives: (a) to characterize the influent streams; (b) to understand the sludge production and characteristics as a function of the specific IWTP design and operations; (c) to characterize the sludges to help define laboratory tests; and (d) to select samples at specific locations for laboratory testing. The analyses included: oil and grease; selected anion and cations; phenols; and elemental and proximate analyses of solids. The test methods and the associated ASTM, EPA, and APHA standards are summarized in Appendix A^(4,5).

3. IWTP Sludge Solids Content

The IWTP operations at the various AF-ALCs produce similar metal hydroxide sludges. The OC-ALC IWTP produces a biosludge and an oil separator sludge that are not currently produced at WR-ALC and OO-ALC. The oil contaminants from OO-ALC and WR-ALC are removed by skimmers (or sink-float units) and the oily waste is sent to thickeners in

which the oily waste is mixed with metal hydroxide sludge. The biosludge produced at OC-ALC is mixed with the metal hydroxide sludge. Because of the mixing of the organic sludges (oily sludge and biosludge) with the metal hydroxide sludges, the sludges produced by all the AF-ALC IWTP operations contain an organic portion and an inorganic portion. All the sludges are produced by one of two thickening operations that remove solid contaminants from waste water; the solids contact clarifier (SCC) and the gravity thickener. The solids contact clarifier increases solid particle size by extended contact of larger solids particles with the fine suspended solids that are introduced into the process from the previous IWTP treatment operation. Gravity settling utilizes the difference in densities between water and the suspended particles in a dilute sludge to remove the particles into a concentrated thick sludge. The final sludges of each IWTP are either disposed or pressure filtered to reduce the sludge volume. The three AF-ALC's use pressure filtration to dewater some of the thickened sludge they produce.

Sludges produced by thickening operations at the IWTP operations vary significantly in their solids content because they are influenced by the maintenance workload and by the length of the periods between sludge discharges which are intermittent. Because each sludge is discharged from thickeners over a period of two to four weeks, the composition of the sludge solids is not expected to vary as greatly as the solids content of the sludge samples. The data in Appendix B are for single samples taken for analysis. Additional data on solids content were collected during the bench scale filtration experiments. Table 4 provides the solids content of the metal hydroxide sludges and the thickened sludges of the three IWTPs. The OC-ALC IWTP also produces an oily sludge (IWTP#5) and a biosludge (IWTP#10) which are discussed as part of the characterization of OC-ALC sludges in Part C since the WR-ALC and OO-ALC IWTPs do not produce these sludges.

TABLE 4. SOLIDS CONTENT OF METAL HYDROXIDE AND THICKENED SLUDGES OF OC-ALC, WR-ALC AND OO-ALC.

AF-ALC Name	Metal Hydroxide Stream		Thickened Sludge		Filter Cake	
	Stream number	Total solids (percent)	Stream number	Total solids (percent)	Stream number	Total solids (percent)
OC-ALC	8	0.8 - 1.1	11	7.5 - 11.5	12	30 - 32
WR-ALC	15	3.4	17	5 - 7	19	30 - 32
OO-ALC	N/A ^(a)	N/A ^(a)	6	7-11	7	28-30

^(a) N/A: Not Analyzed.

4. IWTP Sludge Organic Content

The metal hydroxide sludges at OC-ALC and OO-ALC contain a large fraction of organics as shown in Table 5, based on volatiles content of the sludge solids. (The analysis of the sludge in terms of the dry matter composition allows the elimination of interference from the variability in the solids content that is largely related to the timing of the sample collection.) On the other hand, the WR-ALC sludges are predominantly inorganic and more characteristic of metal hydroxide sludges^(6,7,8). The organic material in the sludges at OO-ALC and WR-ALC is largely oil, since the oil-water separator sludge is mixed with metal hydroxide sludge and since there is no biological sludge in these plants. The organic portions of the OC-ALC sludges is predominantly biological as biosludge is inadvertently recirculated to the head of the IWTP and since the oily sludge is separately discharged.

**TABLE 5. COMPOSITION OF METAL HYDROXIDE AND THICKENED
SLUDGES OF OC-ALC, WR-ALC, AND OO-ALC.**

AF-ALC Name	Metal Hydroxide Stream		Thickened Sludge		Filter Cake	
	Stream number	Volatile organic material (percent, dry basis)	Stream number	Volatile organic material (percent, dry basis)	Stream number	Volatile organic material (percent, dry basis)
OC-ALC	8	42 - 65	11	61 - 72	12	N/A ^(a)
WR-ALC	15	5.5 ^(b)	17	1 ^(b)	19	15
OO-ALC	NA ^(c)	NA ^(c)	6	25-45 ^(d)	7	25-45 ^(d)

(a) Not analyzed.

(b) Based on the assumption that total volatiles = 5 X TOC.

(c) Not applicable.

(d) Estimated based on petroleum hydrocarbon content.

C. SLUDGE CHARACTERIZATION AT OC-ALC

At the Oklahoma City ALC (OC-ALC) located at Tinker AFB, Oklahoma, the waste water is treated at the IWTP to reduce the toxic (RCRA) metals, phenol, total suspended solids (TSS), fat, oil, and grease (FOG), and organic contaminants contributing to BOD and COD. The treatment processes at the IWTP at OC-ALC produce 135 ton/month (1600 tons/year) of combined biosludge and metal hydroxide sludge, and 110 ton/month of an oil-water separator ("oily") sludge. The IWTP process diagram, shown in Figure 2 was prepared based on information obtained through interviews with IWTP personnel. The results of analysis of IWTP streams are given in Table B-1 in Appendix B.

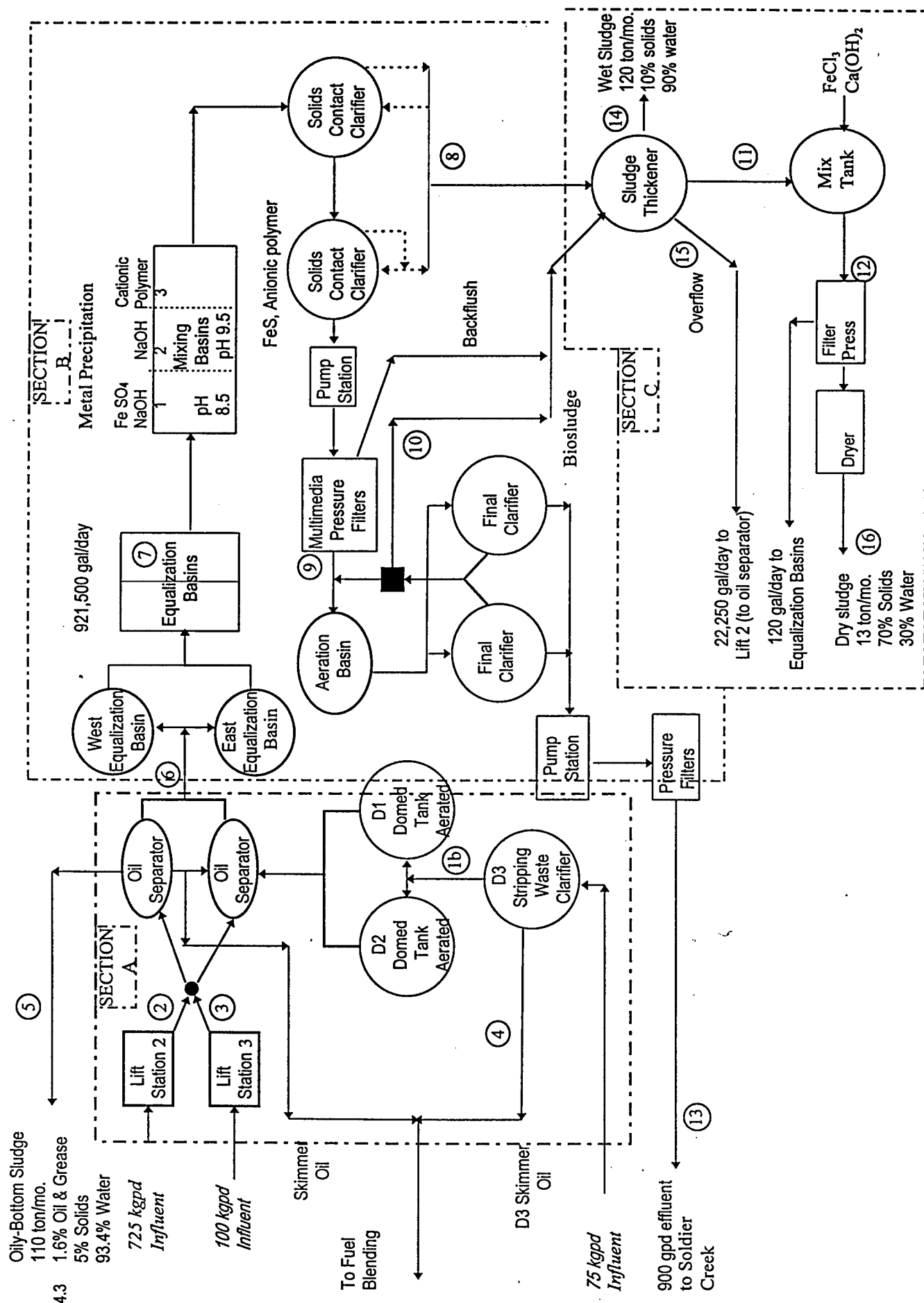


Figure 2. Process Flow Diagram for Tinker AFB (OC-ALC) IWTP.

The major findings of the sludge characterization and the IWTP analysis for OC-ALC are as follows:

- The metal hydroxide sludges (IWTP#8 and IWTP#11) contain a significant quantity of organic matter which includes both biosolids and oil.
- Concentrations of RCRA metals and phenol in the waste water are reduced significantly prior to the IWTP operations designed to remove them and their precipitates appear in the sludge from the initial oil-water separation step.
- Hexavalent chrome (Cr^{VI}) concentrations in the waste water stream are reduced to within NPDES requirements before treatment by ferrous sulfate.
- Biosolids apparently circulate through the IWTP and appear in all the IWTP sludges.
- Oily sludge samples contain relatively little (< 3 percent) oil and most samples filter well, although typical industrial oil separator sludge are composed largely of oil and are very difficult to filter.
- Excess ferrous sulfate is added to the waste water during the metal precipitation stage in quantities 5 to 20 times higher than the theoretical amount required and therefore, constitutes a large portion of the waste sludge from the metal precipitation step.

1. Summary of IWTP Operation at OC-ALC

The IWTP at OC-ALC treats approximately 900,000 gallons per day (900 kgpd) of waste water. Influent to the IWTP are the aircraft painting and paint stripping waste (about 75,000 gpd) and waste water from cleaning/degreasing, plating, and other surface finishing operations (about 850,000 gpd). The painting and stripping waste is first sent to an oil separator (D3), then to two blending tanks (D1 and D2) and then metered out to the IWTP facilities⁽⁹⁾.

The stripping waste and the other AF-ALC waste water streams enter the IWTP processes at the two oil/water separators. The oil phase skimmed from the oil/water separators is reused as fuel and the separator bottoms are drained and disposed as oily sludge (approximately 110 tons/month). The oil separator effluent is then sent to aerated equalization basins for approximately four days. The equalization basins effluent is sent to three mixing compartments for hexavalent chromium reduction and metal precipitation by ferrous sulfate (FeSO_4) and high alkalinity (by NaOH addition) followed by coagulation by ferrous sulfide (FeS) and an anionic polymer. The waste waters containing the precipitated metal hydroxides are sent to a pair of solids contact clarifiers (SCC) where the metal hydroxide sludge is separated as the bottoms (sludge blanket) and sent to the sludge thickener. The SCC effluent is pumped to pressure filters to remove any remaining particulates. The SCC sludge bed (blanket) is maintained by its recycling to capture any colloidal suspensions. FeS is added to the other clarifier for removing the remaining dissolved solids. The filtrate from the pressure filters is sent to aeration basins where biological degradation of organics in the waste water occurs. The effluent from the aeration basins is pumped to a pair of final clarifiers where biosludge is coagulated and removed to the sludge thickener where it is mixed with the metal hydroxide sludge from the SCC. The effluent from the clarifiers is discharged to Soldier Creek.

The mixed metal hydroxide sludge and biosludge from the sludge thickener are either disposed of as wet sludge or prepared for pressure filtration by treatment with ferric chloride (acidifying coagulant) and lime (filter aid). The treated thickener sludge is sent to a filter press and dryer and then disposed of as dry-sludge. About half of the dry contents in the dried filter cakes result from the added lime and ferric chloride. The thickener overflow is recycled to the oil separators.

2. General Characterization of OC-ALC IWTP Streams

The IWTP at OC-ALC produces two main sludges, an oil separator bottoms sludge (IWTP#5) and a thickened mixture of metal hydroxide and biosludge (IWTP#11). The biosludge is the excess waste activated sludge from the operation of the aerobic biotreatment system and the metal hydroxide is produced from the SCC of the metal precipitation system. A portion of the

thickened mixed sludge (IWTP#11) is filtered with the aid of lime and ferric chloride. All OC-ALC sludge solids contain oil, biosolids and metal hydroxides as shown in Table 6. The organic content of the sludges is particularly similar although the oil content of each sludge is different. The major differences in the sludges is in their solids content. The thickened sludges IWTP#5 and IWTP#11 have a much higher solids content compared to dilute sludges IWTP#10 and IWTP#8. The low oil and metal hydroxide content differentiate the biosludge (IWTP#10) from the other sludges that contain some oil and significant quantities of metals. The presence of a relatively high metal hydroxide concentration in the oil separator bottoms sludge indicates settling of metal precipitates in the oil separator prior to chemical treatment to remove metals. The presence of oil in the sludges IWTP#8 and IWTP#11 indicates that some oil escapes the oil separator at least intermittently.

3. Removal of Metal Contaminants in IWTP Streams

RCRA metals are removed from AF-ALC waste water by metal precipitation and coagulation processes designed for that purpose and by inadvertant precipitation and settling in other processes preceding the metal treatment. The metal hydroxide sludge from the solids contact clarifier (SCC), IWTP#8, contained 0.8 to 1.1 percent solids which is within the normal range for an SCC unit. Although the IWTP#8 sludge contained metal hydroxide, about half of the sludge solids were organic from oil and biosolids. RCRA metals were found to be removed in the oil separator and in the equalization basin as well as the metal treatment facilities. The plant is designed to remove the precipitates from the metal hydroxide sludge by mixing with the waste activated sludge (IWTP#10) and gravity thickening to a concentrated sludge (IWTP#11).

TABLE 6. GENERAL COMPOSITION OF OC-ALC SLUDGES AND SLUDGE SOLIDS.

Sludge:	Oil Separator Bottoms, IW/TP#5	Biosludge, IW/TP#10	Metal Hydroxide, IW/TP#8	Mixed ^(a) , Thickened, IW/TP#11	Filter Cake, IW/TP#19
Total solids (percent total basis)	5 - 7.5	0.11 - 0.5	0.8 - 1.1	7.5 - 11.5	30 - 32
Total volatile solids ^(b)	36 - 70	72 - 100	42 - 65	61 - 72	N/A ^(d)
Biosludge presence (septic odor, slime, "rags", gray dry residue)	Odor, "rags" in separator, gray dry residue	Odor, gray dry residue	Odor, gray dry residue	Odor, slime, gray dry residue	Odor, gray dry residue
Carbon to nitrogen mol ratio ^(c)	N/A ^(d)	6.3	9.5	10.3	N/A ^(d)
Estimated biosludge content in solids		67 - 94	22 - 40	35 - 40	
Oil and grease ^(b) , physical evidence	32	No evidence of oil	13	little oil floating, asphaltic odor	asphaltic odor
RCRA metal hydroxides ^(b)	3.9	0.01 - 0.08	0.6 - 2	2 - 5.5	N/A ^(d)
Iron as ferric hydroxide	N/A ^(c)	1.1	12	11 - 14	N/A ^(d)

^(a) The biosludge and metal hydroxide sludges are first mixed and then thickened.

^(b) Percent of total solids.

^(c) Based on the assumption of the non-biological organics containing no nitrogen.

^(d) N/A = Not Analyzed.

a. **Reduction of hexavalent chromium:** More than two thirds of hexavalent chromium, Cr^{VI} , is introduced primarily from the painting (i.e., the alodine process used for primer) and paint stripping waste water. The Cr^{VI} concentrations in the IWTP waste water streams during the month of October 1995 are presented in Figure 3 (the values are averages of measurements of each stream taken at 2 to 8 hour intervals and reported in the IWTP operation log books for October 1995). The concentration of Cr^{VI} is reduced from 0.43 ppm (composite of IWTP #1b and IWTP #2) at the inlet to the oil separator to 0.25 ppm at the oil separator outlet and 0.045 ppm at the equalization basin outlet. It is rather surprising that nearly 90 percent of the incoming hexavalent chromium is eliminated prior to the unit operation designed for Cr^{VI} treatment. In fact, the daily average hexavalent chromium concentrations in the effluent of the equalization basins during the month of October were well below the NPDES requirement of 0.1 ppm. It is suspected that the beneficial presence of other contaminants, e.g., phenols in D3 stream and recycled biosludge, help remove Cr^{VI} .

b. **Elimination of RCRA metals:** The IWTP at OC-ALC is designed to separate RCRA metals after the equalization basins through precipitation by pH adjustment and treatment with ferrous sulfate. The SCC of the metal treatment system coagulates the metal precipitates and removes them from the main waste water stream as a concentrated sludge (IWTP #8). However, analysis of the sludges revealed that RCRA metals are also removed at the oil separator in sludge IWTP #5. The RCRA metals concentrations in the IWTP streams and sludges are given in Table 7. The portion of each RCRA metal disposed in each of the streams IWTP#11 and IWTP#5 is provided in Table 7 (percentage figures). Some of the metals are settled in the oil separator. These metals may have been in their precipitated form (insoluble fine particles suspended in the water) and settled from the influent in the oil separator.

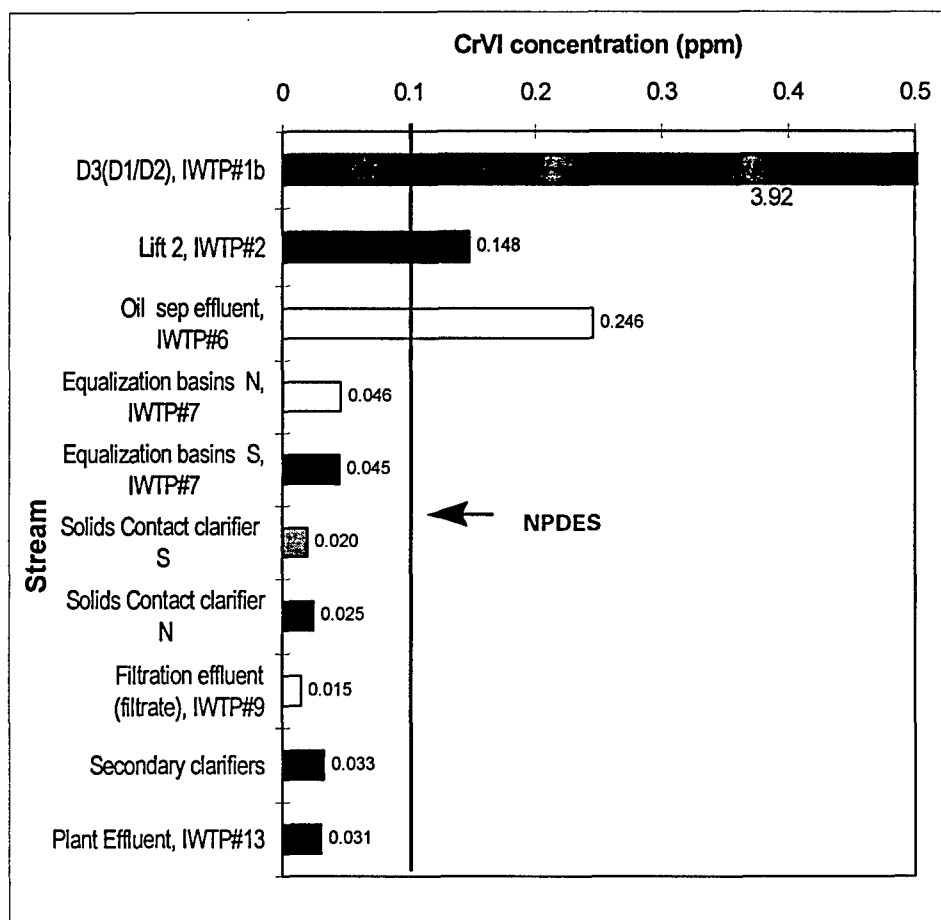


Figure 3. Hexavalent Chromium Concentrations in IWTP Wastewater Streams.

**TABLE 7. RCRA METAL CONCENTRATIONS IN OC-ALC IWTP WASTE
WATER STREAMS AND SLUDGES (COMPOSITE BASIS, ppm).**

Stream Description	Chrome	Lead	Nickel	Cadmium	Copper	Zinc	Iron
D3(D1/D2), IWTP#1b	7.20	0	0.09	0.06	0.09	0.59	
Lift 2, IWTP#2	0.32	0	0.04	0	0	0	
Equalization basin, IWTP#7	0.31	0	0.02	0	0	0	
Final Effluent, IWTP#13	0.0097	0	0.0057	0	0.0025	0.0029	
NPDES limit	0.1	0.1	0.5	0.02	0.05		
Detection limits	0.006	0.01	0.01	0.002	0.003	0.001	
Oil separator sludge IWTP#5	330 15% ^(a)	26 41% ^(a)	193 39% ^(a)	42 38% ^(a)	175		
Metal hydroxide sludge IWTP#8	82	2	13	3	8	7	1260 (87%)
Thickened mixed sludge- IWTP#11	1055 85% ^(a)	11 59% ^(a)	96 61% ^(a)	21 62% ^(a)			8220 (87%)

^(a) Distribution of metal precipitates between oily sludge and mixed sludge.

c. Iron addition for elimination of RCRA metals: Excess iron as ferrous sulfate is added during the metal precipitation process at the OC-ALC IWTP beyond the quantity needed to reduce Cr^{VI} to Cr^{III} and to precipitate the RCRA metals. The iron, added at the IWTP, constitutes most of the metal content of the metal hydroxide sludges (Table 7). Interviews of IWTP personnel revealed that iron is added in excess to assure adequate metal hydroxide coagulation at the SCC through inclusion of metal hydroxides in the large scale matrix that the ferric hydroxide forms. The iron hydroxide constitutes a significant portion of the IWTP sludges IWTP #8 and IWTP #11, particularly if considered with the associated hydration water. Iron complexes are estimated to constitute about a third of the inorganic solids in the sludge IWTP#11 (Table 6).

4. Biosludge Circulation in the OC-ALC IWTP Processes

Biosludge is created at the biotreatment facility in aerated tanks, where bacteria digest organic contaminants such as phenol, and multiply using the organic contaminants as

nutrients. The biosludge is composed of bacteria that are circulated in the secondary solids contact clarifiers as a sludge blanket that promotes the coagulation of bacteria into large clusters. Excess quantities of biosludge from the sludge blanket are removed as stream IWTP#10.

The biosludge, IWTP#10, was very dilute with most samples containing 0.15 to 0.3 percent solids. The carbon to nitrogen ratio of the sludge solids indicates that 70 to 90 percent of the solids in the sludge were biosolids (the biosolids content in Table 6 constitute upper limits). The metal hydroxide sludge, IWTP#8, was analyzed for biosolids concentration through the use of the carbon to nitrogen ratios and was found to contain biosolids that constitute up to 40 percent of the sludge solids.

The analysis of the volatile organics content of various sludge streams, particularly in relationship to IWTP#10 (that is nearly all biosludge), strongly suggests that biosolids are circulated throughout the IWTP. Furthermore, some biosolids may be removed in the oil separator sludge (IWTP#5). A conceptual description of the biosludge flow pattern is given in Figure 4. The circulation of biosludge is attributed to incomplete settling in the sludge thickener, because of the low density difference between the waste water and the biosludge, which impedes gravity settling. The thickener overflow is recycled to the oil separator and it may contain significant concentrations of biosolids. The recirculated biosolids that do not settle in the oil separator are removed in metal treatment (IWTP#8) as well as the thickener (IWTP#11).

Oil separator Metal treatment

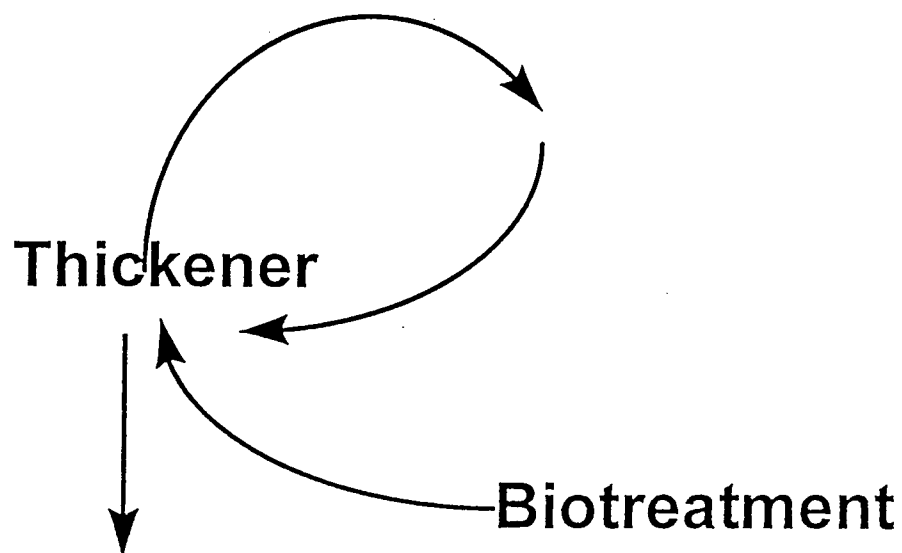


Figure 4. Schematic Flow Diagram of Biosolids Flow at Tinker AFB (OC-ALC) IWTP.

The solids in thickener underflow sludge, IWTP #11, were predominantly organic material (60 to 70 percent on a moisture free basis). Biosolids were estimated to constitute more than half of the organic material according to the carbon to nitrogen ratio in the sludge. Thus, biosludge comprises over 30 percent of the thickened sludge solids.

5. Analysis of Oily Sludge Formation in OC-ALC IWTP Processes

Oil separator bottoms sludge, IWTP#5, is formed at the oil separator from the settling of waste solids from the following sources: (a) primary waste solids from AF-ALC cleaning operations and sweepings; (b) biosolids circulated to the oil separator from the thickener overflow; (c) the precipitation of metal complexes; (d) oil adsorbed on the settling solids. The sludge contained 1.6 percent oil and about 6 percent solids, of which over half were inorganic. The sludge also contained about 1 percent fuel, estimated on the basis of volatile content, TOC, oil/grease, and elemental carbon analysis.

The sludge was unusual for an oil separator bottoms sludge in that there was no evidence of an emulsion in the sludge, it filtered rather easily, and it had a relatively high inorganic solids content. These properties are attributed to two causes: (a) the solids settle in the oil separator as they would in a primary solids settler because the location of the separator at the inlet to the IWTP provides the first opportunity for incoming solids to settle; (b) the large quantities of fuel entering the IWTP from engine testing operations reduces the viscosity of the oily sludge.

6. COD and Phenol Removal in OC-ALC IWTP Processes

The chemical oxygen demand (COD) and phenol concentrations, were also found to drop through the successive IWTP processes, as shown in Figure 5 which is based on the October 1995 average of 2 to 16 measurements per stream per day recorded in the IWTP logs. The IWTP is designed to eliminate phenol by biological aerobic digestion. Although the phenol concentration is reduced in the aerated digester from 25 ppm in its influent (IWTP#9) to only 1 ppm in the stream leaving biotreatment and 0.35 ppm at the plant effluent (IWTP #13), the phenol concentration drops by about two thirds between the oil separator influent (IWTP #6) and the equalization basin effluent (IWTP #7). The COD is reduced in similar fashion, as shown in Figure 6 (based on the October 1995 average of 2 to 16 measurements per stream per day recorded in

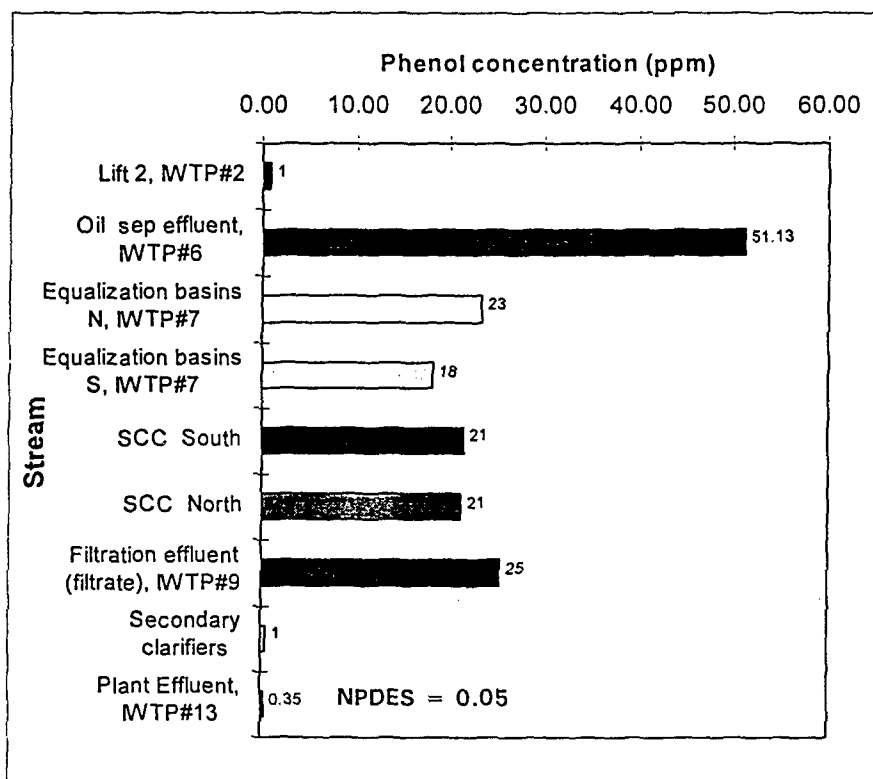


Figure 5. Phenol Concentrations in IWTP of OC-ALC During October 1995.

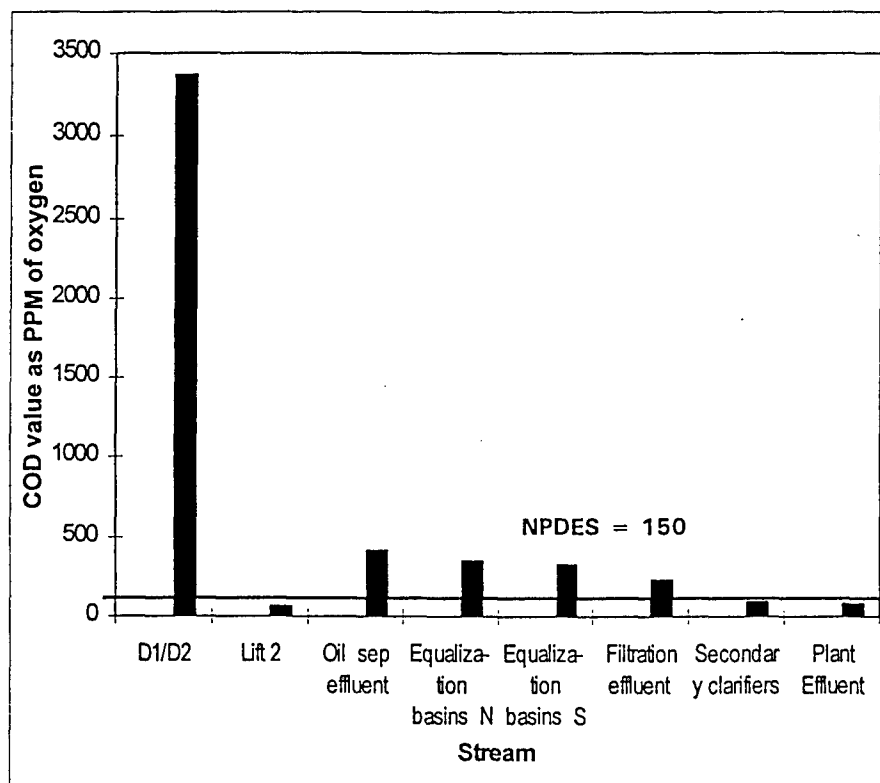


Figure 6. COD Concentrations in IWTP of OC-ALC During October 1995.

the IWTP logs), from about 420 ppm at the influent to the oil separator to 330 ppm in the effluent of the equalization basin. Most of the remaining COD exiting the equalization basin is in dissolved form after passing the sand filter (sand filter effluent, IWTP#9 has 230 ppm COD). The biotreatment process reduces the remaining COD from 230 ppm in IWTP#9 to 91 ppm at the effluent from the SCC of the biotreatment system and is within the NPDES limits.

The COD and phenol behavior in the IWTP streams is normal but for the drop in phenol and COD over the equalization basins, indicating phenol stripping, settling of organic material or biological activity in the aerated equalization basins. The one unusual point that calls for attention is the consistently higher COD value in the oil separator effluent, 420 ppm, compared to the influent COD, 330 ppm (averaged by a COD balance between IWTP#1b and IWTP#2). This indicates that although there is oil and organic solids removal in the oil separator, the incoming recycle streams contain a significant quantity of organic material.

D. SLUDGE CHARACTERIZATION AT WR-ALC

The IWTP at WR-ALC currently generates a single sludge that is predominantly metal hydroxides. The IWTP includes a filter press that has not been operating efficiently due to its age and causes the occasional disposal of unfiltered sludge. This has temporarily increased the sludge disposal rate to 5,800 tons/year. The filter press is scheduled for replacement in the beginning of 1997. Recycling efforts at the AF-ALC have reduced the waste water load at the IWTP from 600,000 gpd to 280,000 gpd. The IWTP is undergoing an upgrade that will include a biotreatment facility and the installation of an additional filter press. The biotreatment facility is expected to produce about 75 tons/month of biosludge (at 10 percent solids). The current IWTP operations are described in the schematics in Figures 7 and 8^(1,10).

The sludges of WR-IWTP contained little organic matter and the major component in the solids is iron hydroxides. The organic content is predominantly attributable to oil. The iron content of the sludge solids is extremely high as shown in Table 8. The iron portion of the sludge solids is consistent between the sludges as they are thickened in various steps. The most significant conclusions of the characterization are as follows:

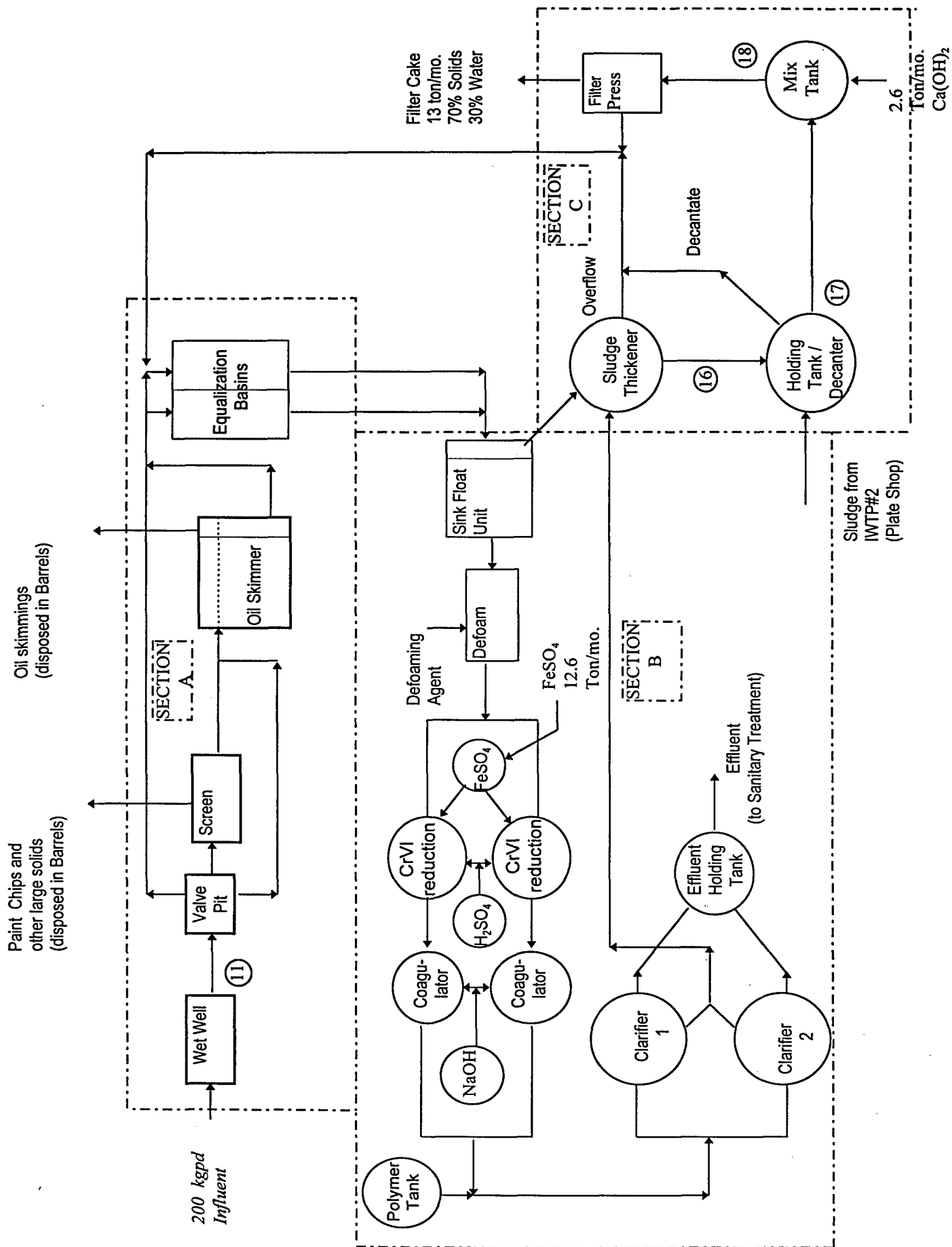


Figure 7. Process Flow Diagram for Warner Robins AFB (WR-ALC) IWTP #1.

Plating Shop Waste

80,000 gal/day

Divided among the streams 22 and 21

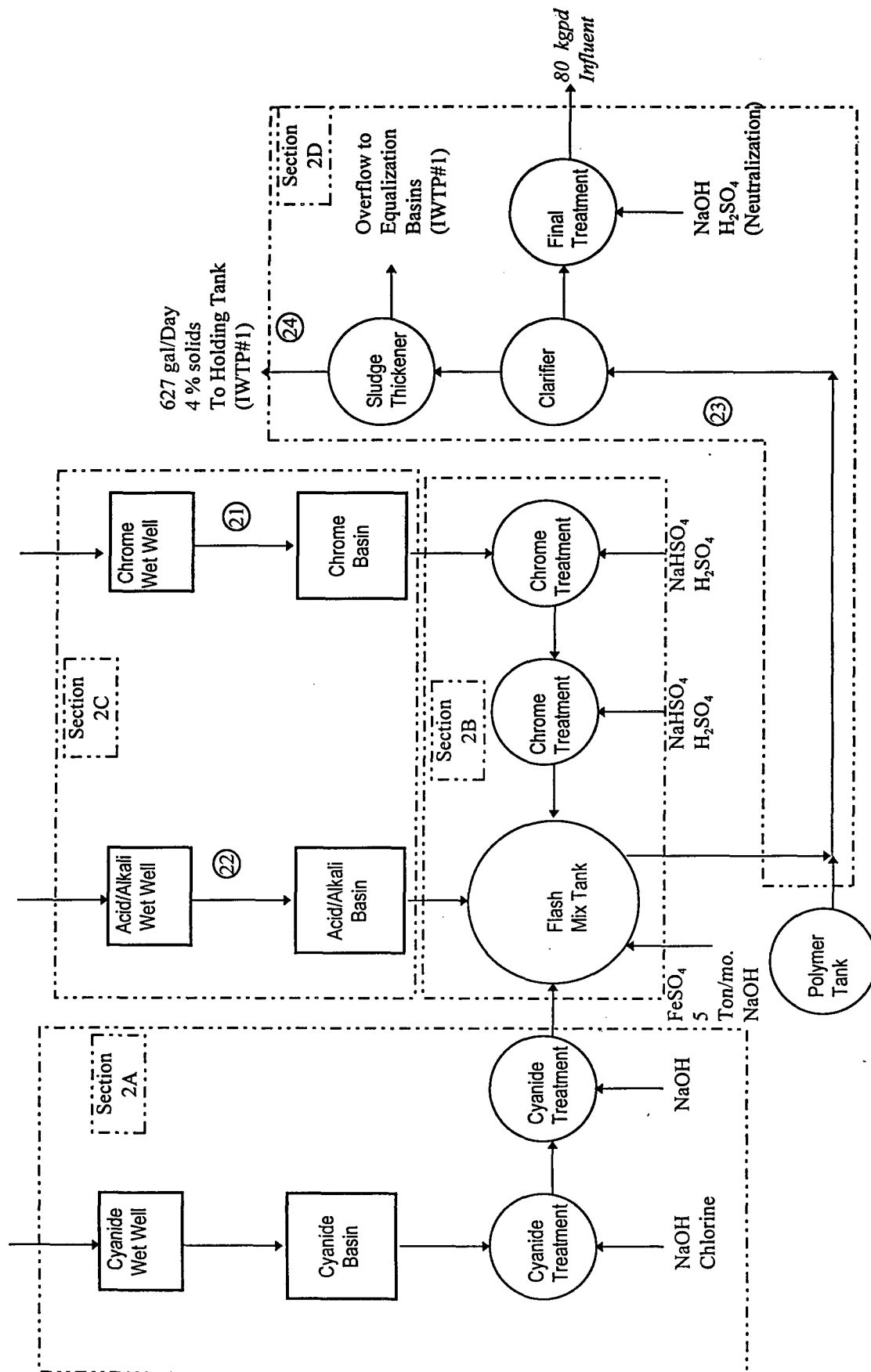


Figure 8. Process Flow Diagram for Warner Robins AFB (WR-ALC) IWTP #2.

- The filter cake contains 31 percent solids.
- Most (over 90 percent) filter cake solids were iron and calcium that were added during treatment.
- The filter cake solids had only 10 percent organics.
- About 75 percent of the chromium is introduced by the plating shop and the balance (25 percent) by the other AF-ALC processes.

TABLE 8. COMPOSITION OF METAL HYDROXIDE AND THICKENED SLUDGES OF WR-ALC.

Sludge:	Metal Hydroxide, IWTP#16	Thickened Sludge, IWTP#17	Filter Cake, IWTP#19
Total solids (percent total basis)	3.4	5 - 7	30 - 32
Total volatile solids ^(a)	5.5	8.6 ^(b)	30
Biosludge presence (septic odor, slime, "rags", gray dry residue)	None	None	None
Oil and grease, (physical evidence, percent)	None	little oil floating 7.4	N/A
RCRA metal hydroxides ^(c)	1	3.3	2
Iron as iron hydroxide ^(c)	70	84	81

^(a) Based on the relationship: total volatiles = 5 X TOC.

^(b) 1.2 in liquid and 7.4 as oil in solids phase.

^(c) Percent of total solids.

1. Summary of the IWTP Operation at WR-ALC

Warner Robins Industrial Waste Treatment consists of two plants, Plant #1 (Figure 7) treating waste water from all shops except the plating shop and Plant #2 (Figure 8) treating waste water from the plating shop only.

a. WR-ALC IWTP Plant #1: Plant #1 handles 200,000 gpd of waste water.

The waste water is fed into a wet well and passes through a screen to separate large solids (e.g., paint chips). The solids are removed and placed in hazardous waste barrels. After screening, the waste water is sent to retention basins for equalization and then pumped to a sink-float tank. Oil and other light contaminants are sent to thickener #1. Waste water from the sink-float unit is pumped to the chrome precipitation tank after the addition of a defoaming agent. Ferrous sulfate is added to the stream to reduce hexavalent chrome (Cr^{VI}) to trivalent chrome (Cr^{III}). The waste water is then sent to a metal precipitation process using alkaline conditions (NaOH addition). Then the process flow is fed to a Solids Contact Clarifier (SCC) where a polymer flocculant is added. The clarified effluent is sent to a holding tank and the sludge is pumped to thickener #1. The sludge from IWTP plant #2 is mixed with the clarifier sludge in thickener #1. The thickener underflow sludge is thickened in a holding tank/settler and then mixed with lime ($\text{Ca}(\text{OH})_2$) in a mixing tank to aid in filtration. The sludge is then sent to a filter press and the pressed solids are disposed as hazardous waste. The filtrate from the press is sent to the head of IWTP #1. The effluent from the sludge thickener is sent to a sanitary sewage treatment plant.

b. WR-ALC IWTP Plant #2: Plant #2 handles 80,000 gpd of plating shop waste water.

Although cyanide and chromium solutions are no longer sent from the plating shop for treatment, separate treatment tanks are available for each of the plate shop solutions: acid/alkali, cyanide, and chrome. The acid/alkali solution is the only plate shop bath solution treated by the plant. Other than this stream, only rinse water enters the plant. Acid or alkali are added to the mix tank to adjust pH for precipitation, and ferrous sulfate is added to precipitate dissolved metals as metal hydroxides. The treated waste water is then sent to a clarifier from which the sludge is

pumped to sludge thickener #1 and the effluent is sent to a final treatment (pH adjustment) and then discharged into the Ocmulgee River.

2. Analysis of WR-ALC IWTP Streams and Sludges

The sludges from the IWTP of WR-ALC (IWTP#17) are metal hydroxide sludges that are formed by the metal treatment systems in Plant#1 and in Plant#2. The major differences between the IWTP facilities at WR-ALC and OC-ALC lie in the absence of a biotreatment facility and a separate oil-water separator at WR-ALC. The process difference is reflected in the character of the sludges of the two IWTP facilities. The WR-ALC sludges contain significantly less organic matter than do the corresponding sludges of OC-ALC. The WR-ALC thickened primary metal hydroxide sludge (IWTP#16) contained 3.4 percent solids, which is significantly higher than the solids content of IWTP#8 at OC-ALC, its equivalent at that plant. The WR-ALC thickened sludge (IWTP#17) had a solids content of 5 to 7 percent, which is lower than that of OC-IWTP#11. However, considering the high organic content of OC-IWTP#11 sludge, the inorganic content is similar. The filter cakes from filter presses at both plants are comparable in their solids content. Detailed data are provided in Table B-2 in Appendix B.

a. RCRA Metal Removal at WR-ALC IWTP: RCRA metals are removed from the IWTP waste water by the metal precipitation process. As shown in Table 9, the concentration of each of the RCRA metals decreased from the plant influent (IWTP#11) to the final effluent (IWTP#15) to below the NPDES limit. Some of the hexavalent chrome reduction may have been performed prior to the chrome reduction step since the chrome reduction influent shows a reduction in the Cr^{VI} and other RCRA metal concentrations relative to the plant influent, IWTP#11. The one anomaly in the IWTP stream metal analysis is the increased iron concentration of the chrome reduction influent (IWTP#13) compared to the incoming AF-ALC waste water (IWTP#11), indicating recycle of iron laden water from the pressure filtration filtrate (the filtrate is often black with iron).

Plating shop waste water, IWTP#21, introduces about 75 percent of the chromium into the IWTP system. The chrome is at a concentration of about 8.5 ppm (mostly in hexavalent

form), which is the major RCRA waste metal in that stream. The influent to Plant #1 contains 1 ppm of chromium (reduced form) which is the major RCRA metal in that stream as well. The sludge from chrome treatment in Plant#2 is mixed in a thickener with the metal hydroxide sludge (IWTP#16) produced by the metal precipitation stage of Plant#1 and oil from the sink-float unit to form the thickened metal hydroxide sludge (IWTP#18).

TABLE 9. RCRA METAL CONCENTRATIONS IN WR-ALC IWTP WASTE WATER STREAMS AND SLUDGES (COMPOSITE BASIS, ppm).

Stream Description	Chrome	Lead	Nickel	Cadmium	Copper	Iron	Calcium
Influent - IWTP#11	1.02	0.07	0.06	0	0.08	3.3	16.8
Influent from chrome well - IWTP#21	8.5	0	0	0	0.06	1.4	15.6
Metal Treatment Influent IWTP#13	0.81	0	0	0.009	0	20.4	17.7
Final Effluent- IWTP#15	0	0.07	0.05	0	0.03	1.3	10.6
NPDES limit	0.1	0.1	0.5	0.02	0.05		
Detection limits	0.03	0.03	0.04	0.03	0.01		
Primary metal sludge - IWTP#16	165	0	0.02	8.7	5	12400	715
Treated sludge, IWTP#17	744	13.5	7	8.4	13	20,300 (88%) ^(a)	784 (3%) ^(a)
Filter Cake, IWTP#19	3,240	72	32	30	76	133,000 (80%) ^(a)	28,500 (15%) ^(a)

(a) Percentages of total metals (RCRA + Zinc +Aluminum +Iron +Calcium + Silicon).

b. Excess Iron and Lime Addition at WR-ALC IWTP: The added iron in the metal hydroxide sludges (IWTP#17 and 18) constituted almost 90 percent of the metal content. RCRA metals were under 1 percent of the sludge solids in the primary metal hydroxide stream (IWTP #16) and only 2 percent of the final filter cake solids (IWTP #19). The thickened sludge, IWTP #18, (that is sent to pressure filtration) was found to have 0.5 percent calcium, corresponding to the addition of 17 percent lime on a dry solids basis; however, interviews with the plant operators indicated that larger amounts of lime were added. The filter cakes (IWTP#19) contained 31.4 percent solids. The combined lime and iron additives (added at the IWTP) were about 95 percent of the filter cake solids.

c. **COD Elimination at WR-ALC IWTP:** The waste water entering IWTP plant#1 (IWTP#11) contains 789 ppm COD and 16.3 ppm oil that are reduced to 314 ppm COD and 8.4 ppm oil at the plant effluent (IWTP#15). This reduction occurs even though there are no operations to reduce COD, and an existing oil separator is not operational (the sink-float unit separates some oil that is sent to the final thickener, but it is not designed as an oil separator). The IWTP upgrades that are currently in construction are to include a biotreatment unit for elimination of COD.

E. SLUDGE CHARACTERIZATION AT OO-ALC IWTP

1. Summary of the IWTP Operation at OO-ALC

The IWTP at OO-ALC, receives about 300,000 gpd of waste water, primarily from electroplating and metal finishing operations. The IWTP process flow diagram is given in Figure 9. The influent is first pumped through a coarse screen to remove large particulates and collected in a wet well. From the wet well, the waste water is pumped to one of three equalization tanks (used sequentially in batches). From the equalization tank, the waste water is pumped to a pH adjustment tank. Cr^{VI} reduction to Cr^{III} is accomplished by sulfuric acid and sulfur dioxide prior to the metal precipitation. In the pH adjustment tank, NaOH is added to precipitate the metals as metal hydroxide. Polymer is also added in the tank as a coagulant. The waste water slurry is then pumped to two inclined plate clarifiers that operate in series. The bottoms from both the clarifiers are pumped to a sludge thickener. The clarifier overflow is treated by H_2SO_4 addition to pH 7. The organic contaminants in the waste water are then removed by four solid bed (Kleensorb™) oil adsorbents that operate in parallel pairs, through an air stripping column, and finally through four carbon adsorption beds that also operate in parallel pairs. The treated waste water is then discharged into the local county sewer. The underflow from sludge thickener is pumped through a filter press and a gas-fired dryer. The dried sludge is collected in gondola cars and transported to a secure hazardous waste landfill by a contractor.

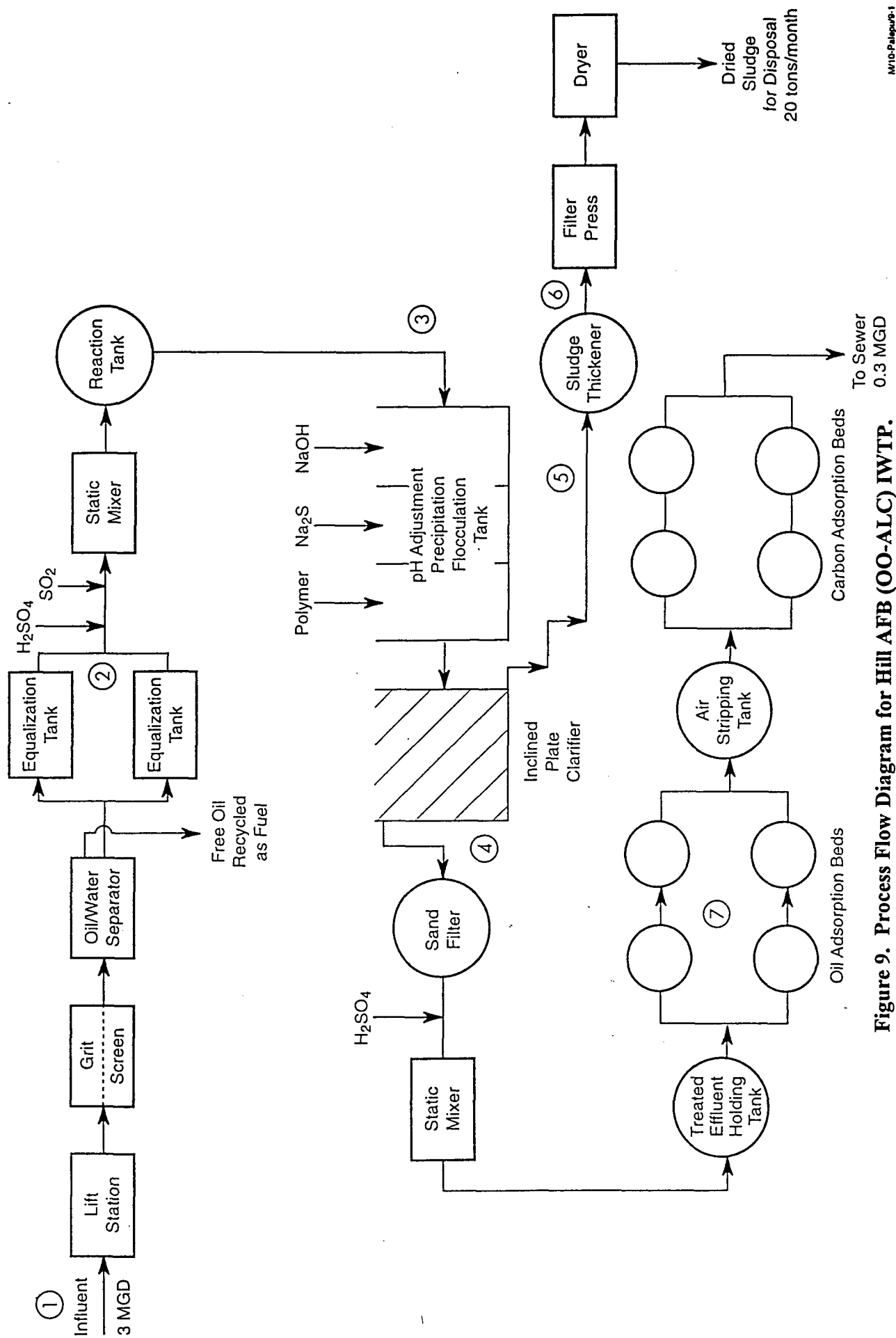


Figure 9. Process Flow Diagram for Hill AFB (OO-ALC) IWTP.

2. Analysis of IWTP Streams and Sludges

RCRA metal content was tested for each of the sludges from the IWTP at OO-ALC. Additional data were obtained from tests performed by the IWTP. The solids content at the sludge thickener is about 11 percent and the thickened sludge is filtered to a solids content of about 28.5 percent. The solids content of the filter cakes is further increased by a dryer that produces a dried cake with a solids content of about 50 percent

Samples of streams 6 and 7 at OO-ALC (sludge thickener underflow and filter cakes from the filter press) were taken and tested for RCRA metal concentrations and general composition. The thickener underflow sludge, stream 6, contained 8.5 percent metal oxides (including calcium and iron in addition to the RCRA metals) and the filter cake, after drying, contained 34 percent metal oxides.

The major RCRA metal contaminant is chromium, which is highly concentrated in the thickened sludge at 3.3 percent, much higher than the concentrations achieved in the sludges from WR-ALC and OC-ALC. The iron and calcium concentrations in the sludge and filter cake are lower than the RCRA metals, so that there is no dilution effect by iron or lime additives. The waste RCRA metal concentrations in the thickened sludge are 30 times higher than in any other thickened sludges tested. Furthermore, the RCRA-metal oxides or hydroxides are a large portion of the waste solids in the sludge, constituting up to 67 percent of the solids, compared to 2 to 5.5 percent at WR-ALC and OC-ALC.

F. GENERAL OBSERVATIONS OF SLUDGE ANALYSIS

The analysis of the sludges at the three AF-ALCs has shown that the metal hydroxide sludges, at OC-ALC and WR-ALC contain large amounts of iron compounds. Iron is added to the IWTP streams in order to reduce Cr^{VI} to Cr^{III} and coagulate fine RCRA metal precipitate particles. The Iron constitutes about 90 percent of the volume of the raw metal hydroxide sludges (IWTP #8 at OC-ALC and IWTP #16 at WR-ALC). The RCRA metals that are removed from the waste water by these processes are only a small portion (less than about 10 percent) of the total metal hydroxide sludge solids. The OO-ALC sludge does not contain much iron as their process for Cr^{VI} reduction is not based on use of ferrous sulfate. The RCRA metal content of

OO-ALC sludges is, therefore, much higher than the sludges from WR-ALC and OC-ALC.

Lime is added in the treatment of the sludges at WR-ALC and OC-ALC, to make up 17 percent and about 50 percent, respectively, of the solids in the filter cakes produced at these sites. The resulting waste for disposal consists of 95 percent additives (dry basis) in the WR filter cakes and it is estimated that over 60 percent of the solids in the OC-ALC filter cakes.

Some oil is present in the thickened sludges from the three AF-ALC IWTPs. The OC-ALC plant produces a separate "oily" sludge stream, but some oil still shows up in the rest of the sludge. The WR-ALC and OO-ALC produce only one sludge so all of the oil and grease in the influent to these IWTPs shows up in the sludge.

Biosludge is present only in the OC-ALC IWTP, however, the upgrade of the IWTP at WR-ALC to include a biotreatment process will produce about 12 tons/month of biosludge (200,000 gpd stream, with 790 ppm of COD).

SECTION V

LABORATORY TESTS ON DEWATERING AND DRYING

Laboratory testing was conducted by Battelle and equipment vendors for dewatering (flocculation and filtration) and drying (evaporation) of the priority sludges. Since the sludges contain 90 to 99 percent water, water removal from the sludges, or dewatering, may be the most effective means to reduce its quantity, aside from the possibility of prevention. The main methods for the removal of water from sludges are^(6,7,11,12): (a) settling by gravity or centrifugal force (e.g., hydrocyclone) (b) flotation; (c) filtration; and (d) evaporation or drying. Since the sludges of concern already undergo settling in the current IWTP processes, experimental efforts were focused on dewatering of the sludges by filtration and by drying.

The IWTP operations at OC-ALC and WR-ALC currently add lime to achieve solids content of 30 to 32 percent in their filtration operations. The effective waste solids content in the sludges is reduced according to the relative quantity of lime that is added. At WR-ALC over 17 percent of the solids in the filter cake were lime; on a lime-free basis, the waste solids concentration in the filter cake was 26 percent. The waste solids concentration, on a lime-free basis, in the OC-ALC filter cakes was 16 percent. The lime addition represents an increase in cost corresponding to the disposal of added lime, chemical purchases and the operating labor required to add the lime.

A. SPECIFIC OBJECTIVES

The task objective was to reduce the total quantity of sludge at the AF-ALCs through improved dewatering and drying techniques. Minimization or substitution of the IWTP chemical additions (such as lime or ferric chloride) may produce improved flocculation and filtration. Thermal drying may further reduce the moisture content and quantity of the waste sludge.

B. PRESSURE FILTRATION

1. Technical Description

Pressure filtration of sludges is based on the flow of water through a porous cloth

that prevents the sludge particles from passing through, thus achieving a separation of the solids from the water (dewatering). The sludge at the cloth surface separates into water flowing through the filter cloth and solids (the solid particles have water adhering to their surfaces and trapped inside the particles). The solids accumulate into a porous cake that increases the resistance to additional water flow. The pores in the cake are the conduit for the water flow so that larger and more numerous pores decrease cake resistance. Sludges with very small particles form cakes with smaller pores that increase the cake's resistance to filtration^(6,13,14).

The effectiveness of pressure filtration is decreased when the properties of the sludge particles or the liquid cause clogging of the pores in the filter cake or the filter cloth (commonly referred to as "blinding"). Particles that are very small may pass through the filter cloth and may not form a cake at all. Small particles may also clog the filter cloth and prevent water flow through it. Flexible particles such as biological solids (from waste activated sludge) are deformed under pressure to fill the voids between particles so that the effective pore size is reduced and filtration ceases. Flexible particles also blind filter cloths as they clog the pores of the filter cake and prevent efficient filtration in that way as well. Biosludge and some other sludges such as oily sludge have a layer of highly viscous liquid on the surface of the particles. In the case of oily sludge the heavy oil and grease coating the solid particles causes blinding of the filter cloth by the thick oil, and the oil is also pushed under pressure to fill the pores in the filter cake. Biosludge may form a layer of highly viscous slime on the filter cloth and prevent water flow through the cloth.

The pressure filtration of most sludges can be characterized by the Carman model. The Carman model relates the volume of filtrate, V , filtered from a sludge with solids content c during the filtration time, Θ , to the pressure, P , the cake resistance (per unit thickness), r , the filtration area, A , and the viscosity of the filtrate liquid, μ . The Carman expression (Equation 1) accounts for filter cloth resistance in combination with other factors in an initial resistance R .

$$\frac{\partial V}{\partial \Theta} = \frac{PA^2}{\mu(rcV RA)}$$

[1]

Cake resistance is determined in laboratory pressure filtration experiments at different pressures by the measurement of the filtrate accumulated over the course of filtration (the filtration curve), represented in Figure 10.

Sludge filtration with a commercial filter press begins with a quick initial flow of sludge through the filter at low pressure until sufficient solids are deposited to form a cake. The cake has a resistance, rcV/A that depends on the cake thickness, cV/A , and causes the filtration rate, $\partial V/\partial \theta$, at a given pressure to decrease. As the filter cake fills the chamber, the effective filtration area is reduced until the chamber is completely full, and the pressure required to maintain the filtration rate increases rapidly. Filtration is stopped when the maximum allowable pressure for the filter press or sludge pump is achieved and the filtration rate has decreased to the point that little additional dewatering is possible. A graphic representation of the progression of a pressure filtration is given in Figures 10 and 11.

2. Laboratory Apparatus and Procedure

A JWI three inch laboratory plate and frame filter press was leased from the manufacturer⁽¹⁵⁾. A diagram of the bench filter press is provided in Figure 12. The press is composed of four major assemblies: (a) the sludge reservoir that holds the sludge under pressure and supplies it to the filtration chamber; (b) the pressure filtration chamber where filtration occurs and the filter cake is deposited; (c) the hydraulic ram that supplies 6,000 psi pressure to seal the plates in the press; (d) the clamp that holds the chamber parts together. The press is assembled on the clamp (serves as the filter press frame) with the filter cloths between the 3 inch (2 inches internal diameter) filter chamber and the support plates. The chamber is held together by the hydraulic ram head that is inserted between the clamp screw and the chamber. Sludge is supplied from the sludge reservoir to the filter chamber through a tube. The filtration pressure is supplied externally from a regulated high pressure nitrogen or air cylinder that is connected to a pressure regulator. The sludge reservoir is mounted on top of a vortexer (not shown) that shakes the sludge reservoir to reduce clogging of the feed tube when sludge particles dewater in the reservoir. The filtrate is collected in a beaker placed upon an electronic balance.

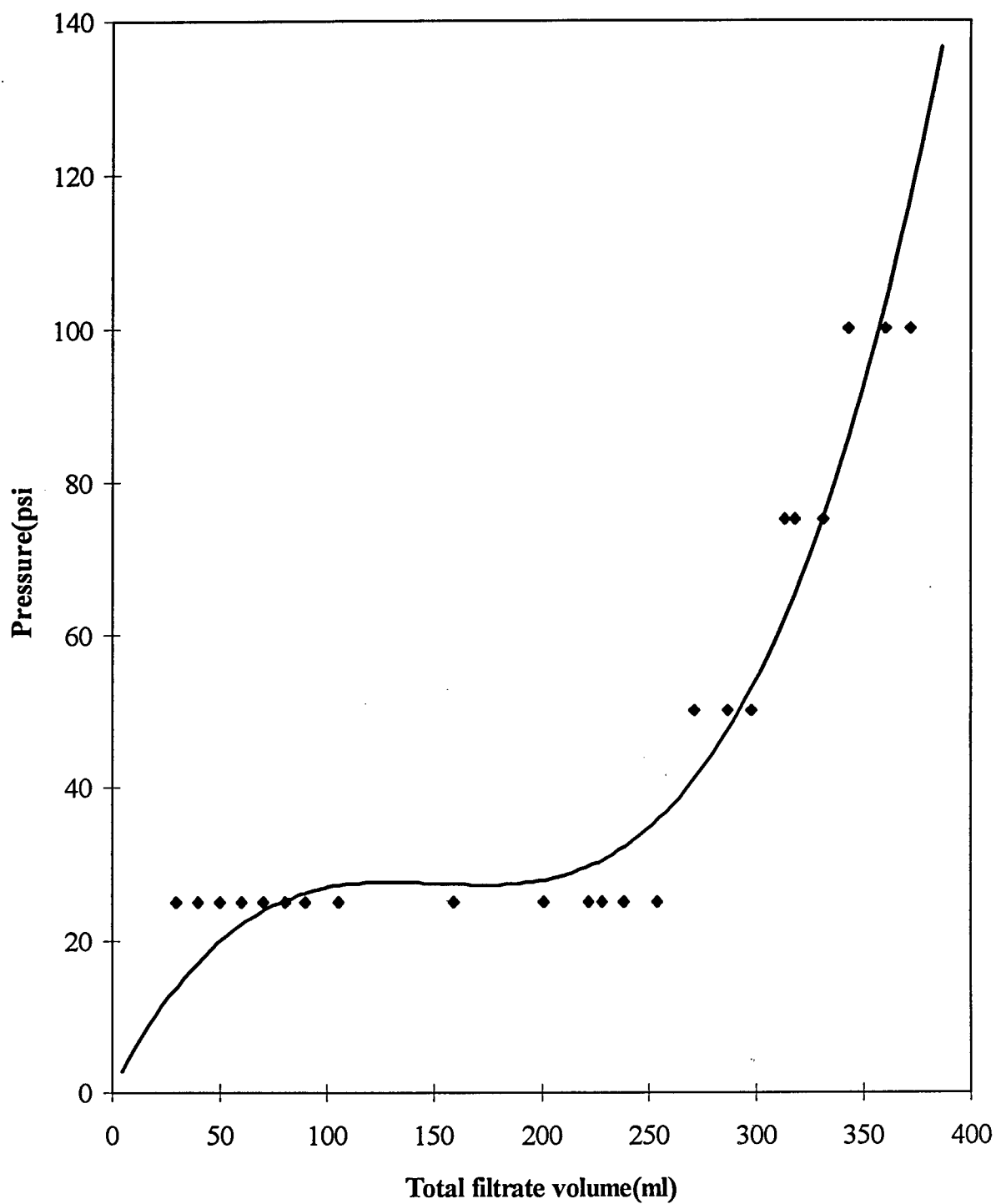


Figure 10. Filtrate - Pressure Curve for Pressure Filtration of WR IWTP#2 Sludge Flocculated with Percol 727.

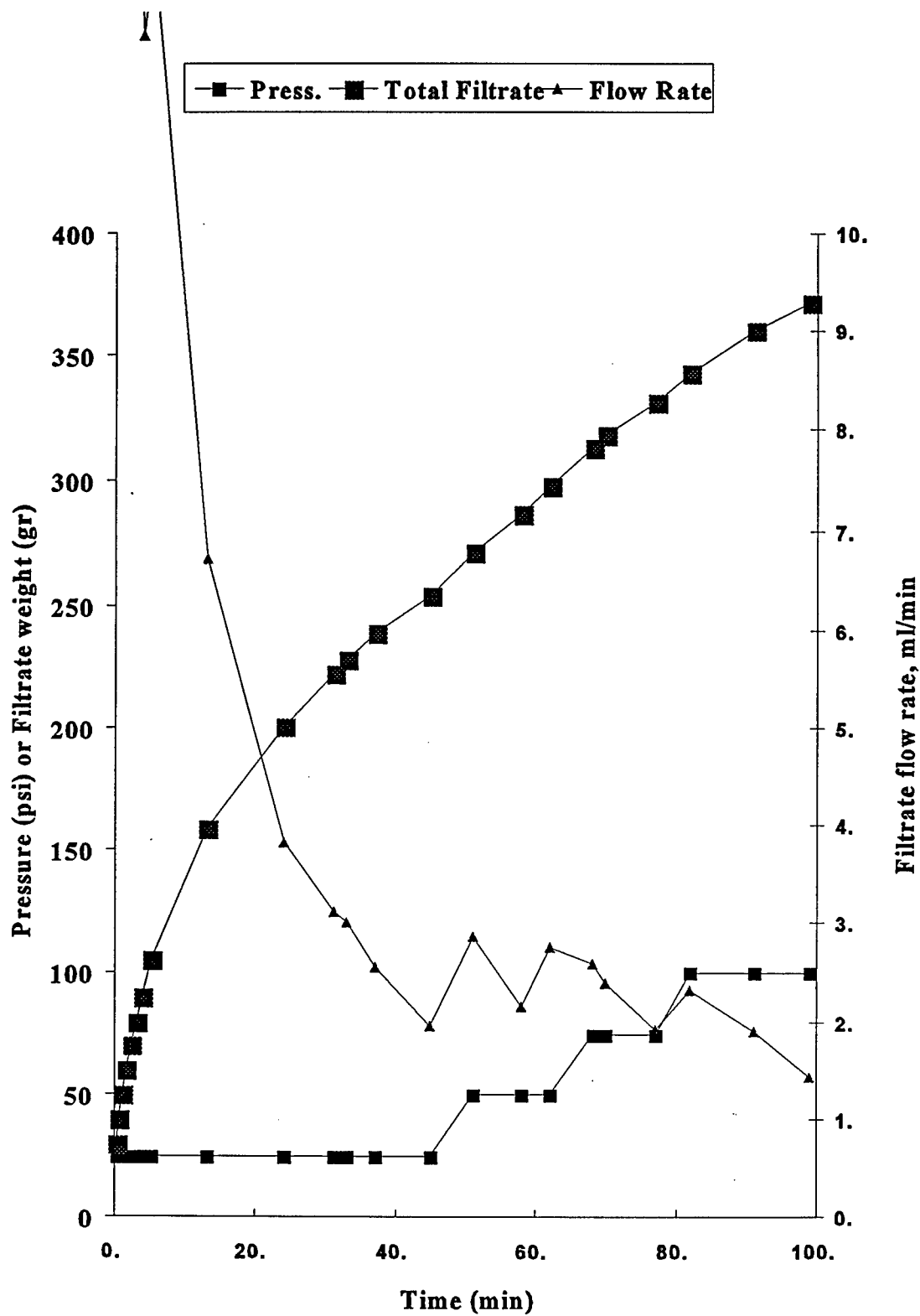


Figure 11. Pressure Filtration Curve of WR IWTP #2 Sludge Flocculated with Percol 727.

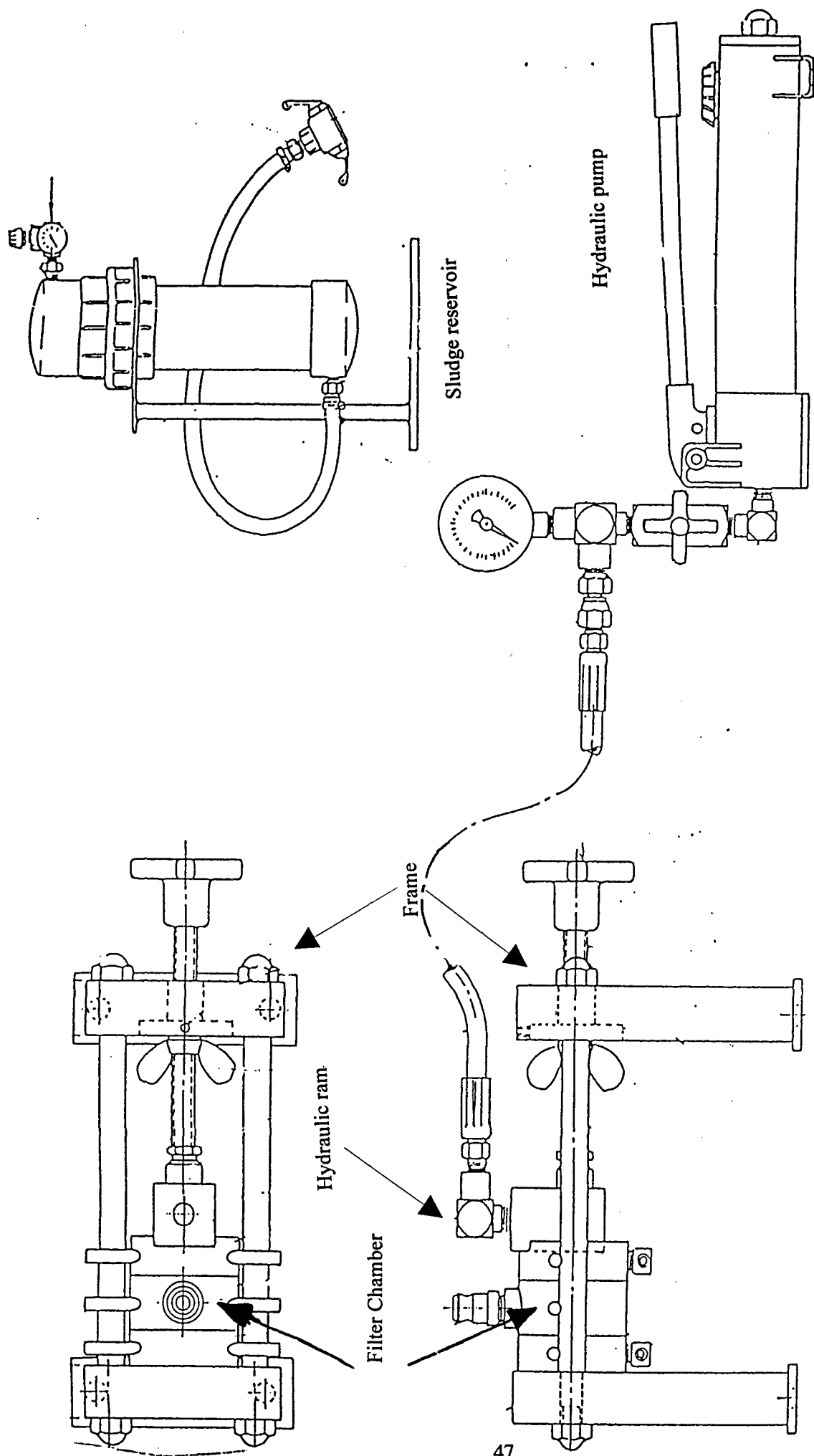


Figure 12. Laboratory Plate and Frame Filter Press.

A typical pressure filtration run begins with assembly of the end plates and the filter chamber on the press frame with the filters in the gaps between the end plates and the filter chamber with the smoother side oriented towards the chamber. Then the hydraulic ram head is inserted and the pump set to 6000 psi. The sludge reservoir is filled with sludge or precoat solution and its top assembled. The appropriate pressure is reached by setting the pressure regulator (at 10 psi when running a precoat). The pressure filtration proceeds from the introduction of pressurized gas to the reservoir until the end point criterion is reached (filtration rate of 2 ml/min or less unless otherwise specified). The pressure is then raised to the next level. Most runs were conducted at pressures of 25, 50, 75, and 100 psi.

3. Use of Flocculants and Filter Aids in Pressure Filtration

Pressure filtration of sludges may be enhanced by the use of filter aids and chemical treatments. Filter aids prevent the clogging of the pores in the cake or in the filter cloth. The common filter aids are the following^(6,8):

- (1) Lime ($\text{Ca}(\text{OH})_2$) raises the pH of the sludge and coagulates it so that the particle size in the sludge is larger. Lime also enhances the cake porosity because of its loose packing.
- (2) Diatomaceous earth is a finely ground, high silicate material that has a uniform particle size and packs loosely. It can be used to enhance cake porosity, but because of its cost it is commonly used as a precoat to protect the filter cloth from clogging.
- (3) Fillers such as rice husks and sand are used occasionally to increase cake porosity and improve filtration.

Filter aids reduce filtration time and increase the solids content of the cake. However, they add to the overall quantity of solids. The filter aids may constitute up to 70 percent of the solids in a filter cake and may increase the overall sludge volume for disposal.

Flocculants and precoat are used in small quantities adding less than 1 percent to the overall quantity of sludge solids for disposal.

a. Flocculation

The use of polymeric flocculants (polyelectrolytes) was investigated to improve dewatering of various sludges. These polymers have a high molecular weight polymer backbone and active groups that can hold a charge in an aqueous environment and cause flocculation by charge neutralization and by bridging between particles. The flocculants are categorized according to the charge of their active groups^(8,16-19). Cationic polymers are positively charged and anionic polymers are negatively charged. Thus, metal hydroxide sludges, that carry a positive charge are often flocculated with anionic flocculants. The flocculating polymers are available at a variety of molecular weights and charge density (the percentage of the active sites that are charged). The charge and molecular weights of flocculants may be selected for specific performance. Lower charged particles may be used for flocculating particles with lower charges. High molecular weight flocculants are necessary for the control of very small particles, very low molecular weights are sufficient when only coagulation by charge neutralization is required⁽¹⁶⁻²⁰⁾.

To effectively mix these polymers with sludge, very dilute solutions of 500 to 1,000 ppm of flocculant must be prepared. Since most of the flocculant is adsorbed onto sludge particles, there is only a low concentration of free polymer in the water phase of the sludge and therefore only a small rise in viscosity of the final sludge mixture. However, if excess polymer is added, well beyond that needed for the complete flocculation of the sludge solids, the concentration of free polymer molecules is increased and viscosity rises quickly with each addition of excess polymer (see Figure 13). High viscosity causes blockage of the dense filter cloths used in pressure filters and prevents filtration. When too little polymer is added not all the particles are flocculated and some fine solids remain in the sludge and increase the resistance of the filter cake and may blind the filter cloth. Also, the flocs may not have sufficient strength under pressure filtration conditions. Thus, there is an optimal dosage (loading) of polymer needed for each sludge. Typically, the polymer loading, given in pounds of polymer per ton of dry sludge solids, should be within about 20 percent of the optimal to get satisfactory results.

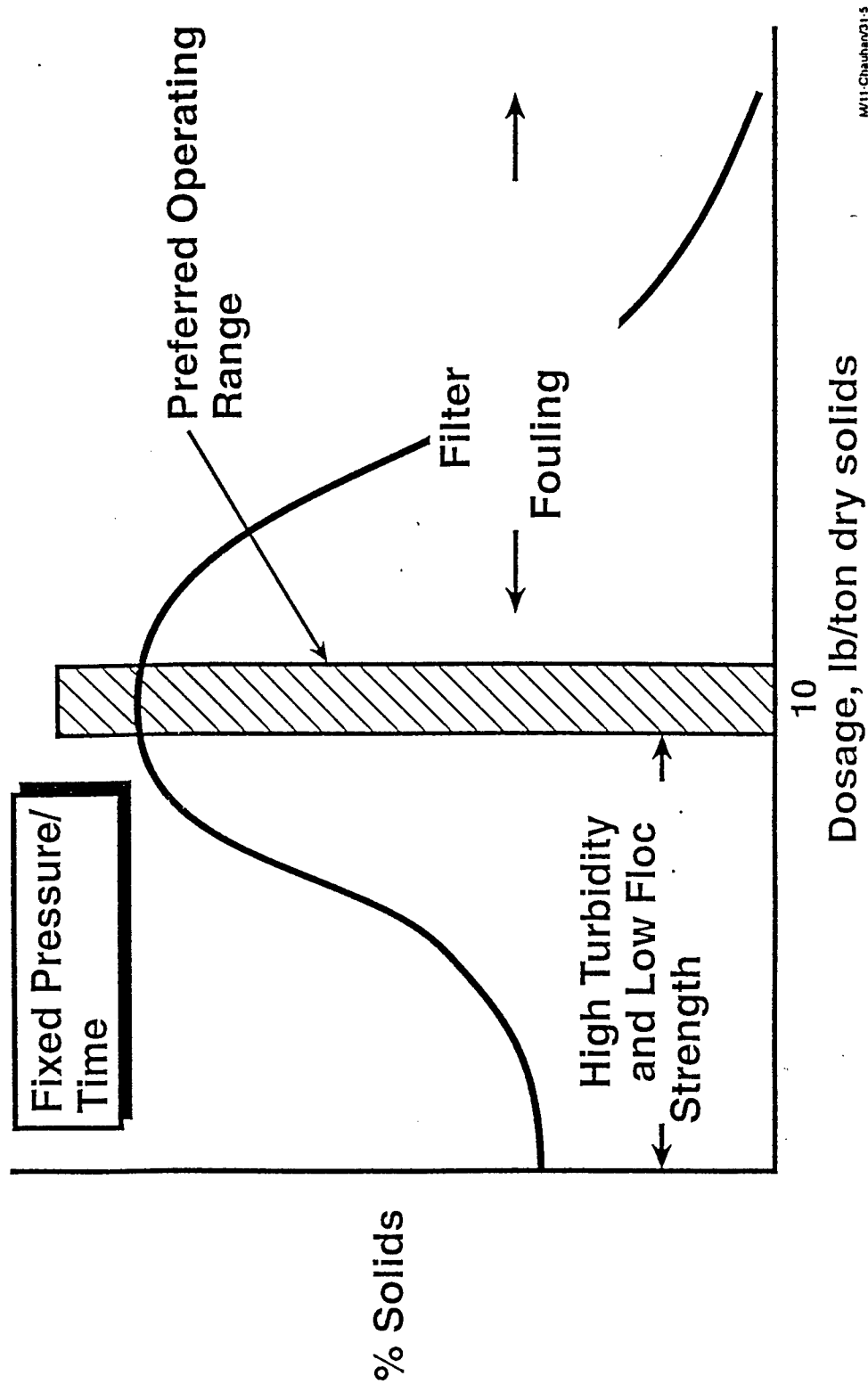


Figure 13. Flocculant Dosage Effect on Solids Content of a Filter Cake.

b. Precoat

Precoats are highly porous, thin coatings deposited on the filter cloth to prevent blinding by loose fine particles, biological slime or heavy oils or greases. The most common precoat material is high silicate diatomaceous earth that is finely ground into a uniform particle size. The precoat is deposited on the filter cloth by dispersing the precoat powder in water at 5 percent concentration followed by pressure filtration of the dispersion. Precoats are used at the rate of 0.05 g/cm^2 (0.1 lb/ft^2) and add only about 1 percent, or less, to the overall weight of solids in the filter cake.

c. Flocculation and Dewatering Test Facilities and Procedures

The sludge flocculation testing was performed with 50-100 mL and 500 mL batches of sludge. The smaller-batch tests were conducted in 200 mL beakers utilizing either 50 mL of thick sludge (7 to 10 percent solids such as OC-ALC sludge IWTP#11) or 100 mL of a more dilute sludge (2 to 5 percent solids such as the WR-ALC sludges IWTP#17, and IWTP#2 or the decanted OC-ALC sludge IWTP#8). These tests were used in conjunction with vacuum filtration only for the purpose of polymer screening. The thick sludge was diluted to 100 mL. The sludges were well mixed by a magnetic stirrer and polymer was added using plastic syringes. Flocculated sludges were vacuum filtered for either 15 or 30 minutes, depending on their solids content, using a Whatman #40 paper in a 7 cm Buchner funnel set on a vacuum flask. Vacuum was provided by a vacuum pump capable of producing 25 inches of mercury of vacuum.

The large scale flocculation tests (500 mL batches) were conducted using a stirring mechanism capable of handling six batches at one time and delivering a controlled rotation rate. The stirrer mechanism provided mixing at rotation speeds of 20 to 34 RPM in its low speed range and 50 to 330 RPM in its high speed range. The stirrers could be independently lifted and secured to prevent excess mixing of a well flocculated sludge.

Two stage flocculation tests were performed on OC-ALC sludge IWTP #11 to test the efficacy of this technique. The two stage approach was recommended by some polymer vendors to increase particle size and thus enhance dewatering^(21,22). The two stage flocculations followed the procedure given previously for the small scale experiments. In the first stage, flocculation of the sludge was performed with a polymer loading determined in earlier testing.

A polymer of opposite charge was then used in the second stage to flocculate the sludge, and the procedure for determination of polymer loading was repeated as before. The cationic polymers were added at a characteristic loading recommended by the vendors to avoid overflocculation. A list of polymers tested is given in Tables 10 and 11.

4. Test Results for WR-ALC IWTP #17 Sludge

The IWTP operations at WR-ALC produce two metal hydroxide sludges (IWTP # 17 and IWTP #2) that are currently mixed together and thickened by gravity settling in a thickener tank, followed by decantation in a second holding tank (thickener). A new filter press is to be installed for the filtration of IWTP #2 sludge (estimated to represent about two thirds of the solids in the current, mixed sludge stream) as part of the IWTP upgrade plan. Because this sludge was expected to have somewhat different properties, it was tested in addition to the mixed sludge (IWTP #17) that is currently being filtered. The results for IWTP #17 sludge are provided below.

a. Polymer Screening: A number of anionic polymers were screened for flocculating IWTP #17 sludge. The flocculated samples were dewatered using the vacuum filtration system. The results of the polymer screening are given in Appendix D Table D-1 and a summary of results for the successful flocculants is given in Table 12. The polymers Nalco 7768 and Percol 727 provided the highest solids content in the filter cake after vacuum filtration.

b. Pressure filtration: The vacuum filtration-based screening experiments were followed by pressure filtration tests that are summarized in Table 13. The full test results are given in Appendix D, Table D-2. The tests were performed to determine the consistency of the loading for flocculation with the two polymers with the best performance, and to determine the behavior of the flocculated sludge at different filtration times and when overflocculation occurs. The key results are provided below.

TABLE 10. ANIONIC POLYMERS USED IN FLOCCULATING CATIONIC SLUDGES.

Percol	Cytec	Calgon	Nalco
725	835	Pol-E-Z 675	7768
726	836	Pol-E-Z 692	
727	837	Pol-E-Z 6500	
	870		
	1820		
	1883		
	1839		
	1885		
	866		

TABLE 11. CATIONIC POLYMERS USED IN FLOCCULATING ANIONIC SLUDGES.

Percol	Cytec	Calgon	Nalco
FS 25:	1598	WT 2640	7194
775	1594	WT 2354	94WP078
767	1596		7196
778			
FS 40:			
775			
767			
778			

**TABLE 12. RESULTS OF POLYMER SCREENING FOR
WR-ALC SLUDGE IWTP #17. (Solids Content
5.1 to 5.3% Diluted to 4.8% to 4.9%).**

Sample Date	Polymer	Polymer Loading lbs/ton(DS)	Comments	Effect	Solids content in filter cake
1/25/96	Cytec 836A	5.9	Large Flocs	Flocculated	10.7%
1/25/96	Cytec 837A	5.9	Very Large Flocs	Flocculated	10.9%
1/25/96	Cytec 866A	7.8	Large Flocs	Flocculated	10.1%
1/17/96	Nalco 7194	15.7	Maximum loading	Not sure	11.8%
4/8/96 and 1/17/96	Nalco 7768	11.6 to 15.7		Flocculated	10.6 - 12.9%
1/25/96	Percol 725	2.5	Large Flocs	Flocculated	12.7%
4/8/96 and 1/25/96	Percol 727	2.9 to 3.1	Small Flocs	Flocculated	13.4%

**TABLE 13. RESULTS OF PRESSURE FILTRATIONS FOR WR-ALC
SLUDGE IWTP #17 WITH DIFFERENT POLYMERS.
(Solids Content 5.3% Diluted to 4.9%).**

Sample date	Polymer	Loading lb/ton(DS)	Criterion (mL/min)	Filtration time (min)	Turbidity (NTU)	Solids content	Specific resistance (X10 ⁷ sec ² /g) at 25 psi
Apr-96 and Jan-96	Nalco 7768(E)	9 to 14	2	75	13 to 104	23 - 24%	200 - 235
Apr-96	Nalco 7768(E)	14.8	1.5	85		23.5%	180
Apr-96	Nalco 7768(E)	13.9	1	175		26.3%	293
Apr-96	Percol 727(P)	2.4 - 3.1	2	65 - 86	34 - 64	21.5 - 25.9%	130 - 160
Apr-96	Percol 727(P)	3.3 - 3.8	1.5	135 - 175	27	26.8 - 28.7%	143 - 153
Apr-96	Percol 727(P)	3.8	1	175	3.5	29.2%	148
Jan-96	No treatment		1	240		27.1%	
Apr-96	Percol 727(P)	4.3	1.5	140		28.1%	184
Jan-96	Nalco 7768(E)	18.0	2		28	20%	

- (1) *Polymer performance:* The specific resistance of the sludge was lower when treated with Percol 727 (about $150 \times 10^7 \text{ sec}^2/\text{g}$ at 25 psi) than its resistance after treatment with Nalco 7768 (about $210 \times 10^7 \text{ sec}^2/\text{g}$ at 25 psi).
- (2) *Comparison to untreated sludge:* Sludge treated with Percol 727 was compared to untreated sludge in a long filtration test using the 1 ml/min filtration criterion for operating pressure adjustment. The treated sludge took 3 hours and achieved 29.2 percent solids content. The untreated sludge took 4 hours to filter and resulted in a solids content of only 27.1 percent. The treatment by Percol 727 cut the filtration time required for achievement of the same solids content by 40 percent (e.g., 27 percent solids could be achieved in a 2.5 hour filtration instead of 4 hours).
- (3) *Filtration time effect:* The effect of extending of the filtration time from 75 minutes to 175 minutes was an increase of the solids content of filter cakes of flocculated sludges from 23.5 percent to over 26 percent using Nalco 7768, and from about 24 percent to over 29 percent using Percol 727.
- (4) *Determination of overflocculation loading:* The overflocculation experiments resulted in higher resistance for the sludge treated with Percol 727 at a loading of 4.3 lbs/ton(DS) and a lower final solids content for the sludge treated with Nalco 7768 at a loading of 18 lbs/ton(DS) compared to values achieved at lower loadings.
- (5) *Recommended operating parameters:* The results show that flocculation with Percol 727 is preferable to Nalco 7768. The recommended polymer loadings are 3 to 3.6 lbs/ton(DS) for Percol 727 and 13 to 15 lbs/ton(DS) for Nalco 7768. Under these conditions, the necessity for adding lime can be completely eliminated leading to potential sludge volume reduction of 16 percent.

5. Test Results for WR-ALC IWTP #2 Sludge

a. **Polymer screening:** WR sludge IWTP #2 samples were treated with flocculants that had successfully flocculated IWTP #17 sludge (but for Calgon Pol-E-Z-692). A summary of the results is given in Table 14 and detailed results are given in Appendix D, Table D-3. The sludge flocculated very well, producing uniform, medium size (about 2 mm diameter) flocs. Vacuum filtration of the flocculated sludge resulted in cake cracking before the targeted 15 or 30 minutes test time elapsed. Since cake cracking occurs at the end of the filtration, the solids content of the filter cakes was not considered a reliable guide for selection of flocculant and determination of flocculant loading. Flocculated sludge samples were then pressure filtered, as discussed below, to detect differences in flocculation behavior with the different flocculants.

b. **Pressure filtration:** The pressure filtration tests were performed to determine the best loading for flocculation using the polymers with the best performance, and to determine the behavior of the flocculated sludge. The results are summarized in Table 15 and the full test results are given in Appendix D, Table D-4. The key results are discussed below.

- (1) *Polymer performance:* The specific resistance of the sludge was lower when treated with Percol 727 (about $80 \times 10^7 \text{ sec}^2/\text{g}$ at 25 psi) than its resistance after treatment with Cyttec 1820A (about $110 \times 10^7 \text{ sec}^2/\text{g}$ at 25 psi). The solids concentration in the filter cakes was about the same (29 percent) for the two polymers..
- (2) *Comparison to untreated sludge:* Sludges treated with Percol 727 and Cyttec 1820 were compared to untreated sludge. The untreated sludge stopped filtering after 75 minutes (the filtration of untreated sludge was extended beyond the 2 ml/min stop criterion) while the treated sludges continued to filter until 80 to 100 minutes. The solids content achieved was over 29 percent with the two treated sludges and only 25.5 percent for the untreated sludge. These results basically confirm that the untreated

**TABLE 14. RESULTS OF POLYMER SCREENING FOR
WR-ALC IWTP #2 SLUDGE. (Solids Content
3.4% Decanted to 6.9%).**

Sample Date	Polymer	Polymer Loading (lb/ton _{DS})	Effect	Solids content in filter cake	Filtrate Turbidity (NTU)
4/29/96	Calgon, Pol-E-Z-692	6.0 - 9.0	Flocculated	14.2 - 15.6%	0.8 - 1.2
4/29/96	Cytec 1820A	13.7 - 18.7	Flocculated	11.5 - 13.5%	0.9 - 4.1
4/29/96	Cytec 836A	2.4 - 3.0	Flocculated	14.4 - 15.9%	0.8 - 1.4
4/29/96	Percol 727	1.5 - 2.4	Flocculated	15.0 - 16.7%	1.1 - 1.3

**TABLE 15. RESULTS OF PRESSURE FILTRATIONS FOR WR-ALC
IWTP #2 SLUDGE WITH DIFFERENT POLYMERS.
(Solids Content 3.4% Decanted to 6.9%).**

Polymer	Loading (lb/Ton _{DS})	Filtration time (min) ^(a)	Number of filter cloth reuses	Solids content	Specific resistance (X10 ⁷ sec ² /g) at 25 psi
Calgon, Pol-E-Z-692	8.8 - 16	80		25.9 - 26.1%	190 - 204
Cytec 1820A	18.4	85		29.3%	108
Cytec 837	3.5	90		25.9%	124
Percol 727	3.6	99		29.1%	81
No treatment		75		25.5%	180
Cytec 1820A	^(b) 14.0	80	4	28.3%	159
Cytec 1820A	^(b) 15.4	80	3	28.9%	158
Cytec 1820A	^(b) 13.8	80	2	28.9%	158
Cytec 1820A	^(b) 11.9	80	1	29.0%	203

^(a) All filtrations were conducted using a 2 ml/min criterion.

^(b) Minimum loading for complete flocculation.

sludge does not filter satisfactorily, which is why WR-ALC currently uses lime as a filter aid. What the results of this study show is that the use of polymeric flocculant can lead to elimination of lime addition and thus result in sludge volume reduction.

- (3) *Filtration time effect:* The effect of extension of the filtration time was not tested.
- (4) *Determination of filter fouling effects:* Sludges were flocculated with Cytec 1820 to the point of complete flocculation and filtered repeatedly on the same filter cloth (four repetitions). The experiments resulted a slight drop in the solids content from over 29 percent to 28.3 percent after four reuses. The specific resistance was higher than that of the sludge flocculated with a 10 percent excess polymer. Specific resistance was largely consistent between the runs, as expected from filtration theory (the specific resistance is determined from the change of total resistance with cake thickness and is independent of the filter cloth resistance).
- (5) *Recommended operating parameters:* The results show that both Percol 727 and Cytec 1820 are suitable flocculants. The recommended flocculant loadings are about 3.5 lbs/ton(DS) for Percol 727 and 15 - 18 lbs/ton(DS), for Cytec 1820.

6. Test Results for OC-ALC IWTP #11 Sludge

The OC-ALC sludge IWTP#11 was tested for flocculation behavior with a variety of polymers and with combined polymer treatments. The filterability was determined by both vacuum filtration and pressure filtration tests. The sludge was successfully flocculated by a number of flocculants, creating small, soft flocs with most and large flocs with Cytec 836. The

results are presented in Appendix D, Table D-5 and are summarized in Table 16. Most of the vacuum filtration tests indicated that further dewatering beyond that achieved by gravity thickening (about 10 percent solids content) is very difficult. The exceptions to this were Cytex 836 and Percol 725, which gave higher (i.e., 12 to 13 percent) solids content in the filter cake. Most vacuum filtrations were done with a precoat but the precoat had a negligible effect on the final solids content of the sludge. The better polymers required significantly higher loadings than the manufacturer's recommendations.

Although the IWTP#11 sludge measured slightly cationic based on zeta potential measurements, there were some attempts made to flocculate the sludge using cationic polymers. The low particle charge was thought to contribute to the difficulty in flocculating the sludge. This raises the option of increasing particle charge as a possible way to improve flocculation. However, none of the cationic polymers investigated flocculated the sludge successfully. In fact, some flocculants dispersed and homogenized the sludge. Results of these experiments are summarized in Table 17.

A number of vendors recommended the use of a combined treatment by two flocculants of opposite charges. The first polymer was to disperse sludge particles of similar charge and bind particles of opposite charge into flocs. The process was expected to result in a more uniform and higher particle charge that could allow better flocculation by a second polymer of opposite charge. Since the sludge was slightly cationic, the dispersion stage was more readily accomplished by the addition of cationic polymer, and the flocculating polymer was anionic. The results of these experiments are summarized in Table 18.

A similar experiment was conducted using anionic polymer followed by a cationic polymer. This polymer addition strategy tested whether flocculation with a cationic polymer could eliminate the fine solids. The particles were not eliminated completely in any of these flocculation tests and there was no improvement in the 30 minute vacuum filtration compared to direct treatment with the anionic polymers. Results of these experiments are summarized in Table 19.

**TABLE 16. RESULTS OF ANIONIC POLYMER SCREENING
FOR OC-ALC IWTP #11 SLUDGE. (Solids Content
8.9% to 10% Diluted to 5.4% to 5.6%).**

Sample Date	Polymer	Polymer Loading lb/ton(DS)	Effect	Filtration ^(a) Time (min)	Solids content in filter cake	Filtrate Turbidity (NTU)
4/8/96	Cytec 1820A	45.1	Flocculated	15	9.7 %	384
4/8/96	Cytec 835A	1.8	Slight flocculation	15	9.5 %	480
4/8/96	Cytec 836A	3.2 - 3.5	Flocculated	30	12.0 - 12.8%	
4/8/96	Cytec 837A	1.6	Some flocculation			
4/8/96	Percol 725	3.6 - 4.5	Flocculated	30	13 - 13.6%	
1/24/96	Percol 727	3.3	Initial Flocculation	30	8.4%	

(a) Vacuum filtration test.

**TABLE 17. RESULTS OF CATIONIC POLYMER SCREENING
FOR OC-ALC IWTP #11 SLUDGE. (Solids Content
8.9% Diluted to 5.4% to 5.6%).**

Sample	Polymer	Polymer Loading lb/ton(DS)	Effect
1/24/96	Clg polyz6500	4.4	No effect
1/24/96	Cytec 1596	26	Dispersion of particles
1/24/96	Nalco 7194	13.6	No effect
1/24/96	Nalco 7196	21.8	No effect
1/24/96	Percol FS778-40	27.27	No effect
1/24/96	Percol FS775-40	27.27	No effect
1/24/96	Percol FS767-40	27.27	No effect
4/8/96	Percol FS767-25	9.0	No effect

**TABLE 18. RESULTS OF DISPERSION BY CATIONIC POLYMER
FOLLOWED BY FLOCCULATION BY ANIONIC
POLYMER FOR OC-ALC IWTP #11 SLUDGE.
(Solids Content 9.7% Diluted to 3.2%).**

Polymer Stage 1	Polymer Loading lb/ton(DS)	Polymer Stage 2	Polymer Loading lb/ton(DS)	Effect	Solids ^(a) content in filter cake
Cytec 1594	21	Percol 727	2.9	No Effect	
Cytec 1594	21	Cytec 836	1.8	Small flocs	7.93 %
Cytec 1594	21	Cytec 1820	7.0	Flocculation	5.19 %
Cytec 1598	21	Percol 727	2.9	No Effect	
Cytec 1598	21	Cytec 836	2.9	Granular	5.73 %
Cytec 1598	21	Cytec 1820	7.0	Flocculation	6.33 %
Percol 767 FS 25	21	Percol 727	4.1	Flocculation	
Percol 767 FS 25	21	Cytec 836	3.5	Flocculation	
Percol 767 FS 25	21	Cytec 1820	14.0	Flocculation	Did not filter

^(a) Vacuum filtration tests.

**TABLE 19. RESULTS OF FLOCCULATION BY ANIONIC POLYMER FOLLOWED
BY FLOCCULATION OF REMAINING FINE SOLIDS BY CATIONIC
POLYMER FOR OC-ALC SLUDGE IWTP #11.
(Solids Content 9.7% Diluted to 3.2%).**

Polymer Stage 1	Polymer Loading lb/ton(DS)	Polymer Stage 2	Polymer Loading lb/ton(DS)	Effect	Solids content in filter cake
Cytec 1820	12	Nalco 7194	4.6	Flocculation	6.12 %
Cytec 1820	12	Cytec 496	1.2	Large flocs	
Cytec 1820	12	Percol 778 FS 40	7.0	Grainy flocs	
Cytec 837	12	Nalco 7194	7.0	Large flocs	
Cytec 837	12	Cytec 496	1.2	Grainy flocs	
Cytec 837	12	Percol 778 FS 40	7.0	Grainy flocs	
Percol 725	1.3	Nalco 7194	10.5	Flocculation	7.12%
Percol 725	1.3	Cytec 496	1.6	Some Grainy flocs	
Percol 725	1.3	Percol 778 FS 40	10.5	Flocculation	6.56%
Calgon Pol E Z 692	2.8	Nalco 7194	10.5	No Effect	7.12%
Calgon Pol E Z 692	2.8	Cytec 496	1.6	No effect	
Calgon Pol E Z 692	2.8	Percol 778 FS 40	10.5	Flocculation	6.18%

Based on the vacuum filtration screening test results, the preferred polymers were evaluated using the pressure filtration system. A precoat was used in all tests to reduce filter blinding. The data were analyzed in terms of specific cake resistance, which determines the time required to reach a certain cake solids level at a given pressure, and the consistency of the cake. The results, summarized in Table 20, show that Cytec 836 and Percol 725 help reduce the cake resistance, at 15 psi, by a factor of 5 to 10 compared to untreated sludge. Consequently, the time required to increase solids content from 10 percent in thickened sludge to about 16 percent is 2-3 times longer for untreated sludge. However, in all cases, the final filter cake was too fluid to handle. Had the filter cake been easy to handle, the preferred flocculation systems (i.e., Cytec 836 or Percol 725) would have eliminated the use of ferric chloride and lime without sacrificing degree of dewatering.

**TABLE 20. RESULTS OF PRESSURE FILTRATION OF FLOCCULATED
OC-ALC IWTP #11 SLUDGE USING A PRECOAT.
(Solids Content 8.9% to 9.7% Diluted to 5.6% to 7.5%).**

Polymer	Loading lb/Ton(DS)	Solids content	Criterion (mL/min)	Filtration time (min)	Specific resistance ($\times 10^7$ sec ² /g) at 10 psi	Specific resistance ($\times 10^7$ sec ² /g) at 25 psi	Consistency of Filter Cake
Cytec 836	3.6	15.6%	1	77	91	498	Semisolid
Cytec 837	2.7	15.9%	0.5	95	619	1825	Semisolid
Percol 725	2.5	16.6%	0.5	120	354	1107	Semisolid
Percol 725	4	16.1%	1	120			Semisolid
Cytec 1820	25	16%	1	100	190	1074	Semisolid
Cytec 1596 then Cytec 835	26 1.4	14.9%	1	65	378	1419	Semisolid
No Polymer		16.9%		240	978		Semisolid

7. Test Results for OC-ALC IWTP #8 and IWTP #10 Sludges

Since the polymer treatment of the mixed sludge (IWTP #11) was not successful, it was decided to separately treat the metal hydroxide sludge (IWTP #8) and the biosludge (IWTP #10) employing treatment conditions specially suited for the particular sludge. The IWTP #8 sludge was tested for flocculation behavior with a variety of anionic polymers. The sludge was successfully flocculated by a number of flocculants, creating small flocs with most polymers. The results employing pressure filtration are presented in Table 21. The flocculated sludge filtered better than the untreated sludge. The polymers providing the best results were Cytec 837 and Cytec 1820. The specific resistance of the treated sludges at 25 psi did not correlate with the final solids content achieved by the filtration. Because of the great difference between the solids concentrations of the sludge samples, it is the multiple of the specific resistance, r , and the solids concentration, c , that affects the filtration behavior of the sludges. As shown in equation 1, rc correlates with the filter cake solids content obtained in the filtration.

The IWTP #10 sludge was tested for flocculation behavior with cationic polymers. The sludge was flocculated successfully but did not filter well with any of them. IWTP #10 is a waste activated sludge and biosludges are notorious for exhibiting filtration problems. Pressure filtration of biosludge flocculated with Nalco 94WPO78 resulted in only 8.2 percent solids in the filter cake, and another filtration of this sludge, flocculated with Percol 787 FS 40 was stopped due to a lack of filtration after two hours. The filtration of the combined IWTP #8 and IWTP #10 after individual flocculation by Percol 725 and Nalco 94WPO78, respectively, resulted in only 12.9 percent solids after a 3 hour filtration.

It was then decided to try the conventional ferric chloride and lime treatment of IWTP #10 sludge. Using 1 part by weight biosolids to 0.13 parts ferric chloride and 1.3 part lime resulted in a high solids content of 38 percent, of which the biosolids content (on an additives-free basis) was 15.6 percent. Similar results were obtained in a similar experiment with the proportion 1 part by weight biosolids to 0.1 parts ferric chloride and 1.0 parts lime, where the overall solids content was 33 percent and the waste solids content was 15.7 percent.

TABLE 21. RESULTS OF PRESSURE FILTRATION OF FLOCCULATED OC-ALC IWTP #8 SLUDGE.
(Solids Content 1% Decanted to 1.8%).

Polymer	Loading lb/ton(DS)	Solids content ^(a)	Filtration time (min) ^(b)	Specific resistance (X10 ⁷ sec ² /g) at 25 psi	Resistance X solids conc. (X10 ⁷ sec ² /ml) at 25 psi	Turbidity (NTU)
Cytac 837	3	26.0%	145	354	6.3	12.9
Calgon PolEZ 692	9	21.1%	230	237	4.6	24
Cytac 1820	10.9	24.1%	205	264	11.1	9.4
Cytac 1883	11.9	22.5%	170	538	9.1	13
Percol 725	2.5	21.8%	155	570	10.7	
No flocculant		16.6%	105	363	19.5	

^(a) No precoat was used.

^(b) Filtration criterion was 1 mL/min.

In both cases, the filter cake was easy to handle. The combination of ferric chloride and lime treatment of IWTP #10 sludge and anionic polymer treatment of IWTP #8 sludge can thus result in a combined waste solids content of about 20 percent. This was calculated assuming that two thirds of the sludge solids are from the IWTP #8 stream, which can be dewatered to 26 percent solids, and the rest from the biosludge stream, IWTP #10, which can be separately treated and dewatered to 15.6 percent. This represents a 20 percent sludge quantity (mass) reduction compared to current operation where effective waste solids concentration in the filter cake is only 16 percent. At the same time, there are some savings in the proposed process due to a reduction in the amount of ferric chloride and lime used.

8. Technical Evaluation of Dewatering Alternatives

The use of lime at the IWTP operations of OC-ALC and WR-ALC can be curtailed or eliminated entirely by the use of flocculants for the treatment of some of the sludges. Furthermore, the waste sludge quantity can be reduced by using the flocculants tested in this program compared to those obtained by the use of lime.

a. WR-ALC Dewatering Options

The best dewatering performance on IWTP #17 sludge from WR-ALC was obtained with Percol 727 at loadings above 3.3 lbs/ton(DS) and is not very sensitive to loadings above that level. The upgrade program for the IWTP at WR-ALC includes the installation of a new filter press for the separate filtration of IWTP #2 sludge that is produced by the plating shop waste water treatment plant (IWTP #2). IWTP #2 sludge is currently mixed with the Plant 1 sludge and thickened to form IWTP #17 sludge. The sludge may be flocculated easily using Percol 725 and Cytec 1820 at loadings of 3.6 and 14 lb/tonDS, respectively. The repetitive filtration tests for this sludge did not reveal significant degradation of the filtration performance that would require a precoat. The solids content that has been obtained by pressure filtration at 100 psi following flocculation is 29 percent, and we estimate that a solids content over 31 percent solids may be achieved by the use of a 200 psi press.

The waste quantity reductions that may be obtained by the use of flocculants in treating WR-ALC sludges are summarized in Table 22. The simplified block process flow diagrams for the WR-ALC IWTP before and after implementing the proposed process are shown in Figures 14 and 15, respectively. The estimated sludge mass reduction is 9.4 percent if the existing 100 psi press is used. The expected sludge volume reduction for a 200 psi press is expected to be about 16 percent. The proposed process will require the equipment changes shown in Figure 16. The addition of a flocculation system is shown by dotted lines in Figure 16.

TABLE 22. WASTE QUANTITY REDUCTION BY PRESSURE FILTRATION OF FLOCCULATED WR-ALC SLUDGES IWTP #17 AND IWTP #2.
(Basis: 100 Pounds of Thickened Sludge at 5 Percent Solids)

	Current treatment of IWTP#17 filtered at 270 psi 90 min	Flocculation of IWTP#17 filtered at 100 psi 175 min (expected result for 200 psi)	Separation of IWTP#2, filtered at 100 psi 85 min (expected result for 200 psi)
Solids content	31.4 %	29% (31%)	29% (31%)
Additive	Lime	flocculant	flocculant
Additive quantity added, lbs	1	0.075	0.075
Final waste Quantity, lbs	19.1	17.3 (16.1)	---
Waste quantity reduction compared to current treatment, %		9.4% (16%)	---

b. OC-ALC Dewatering Options

Waste quantity (mass) reductions may be achieved at OC by the separate treatment of IWTP #8 and IWTP #10 rather than their combination into IWTP #11 as shown in Table 23. Current operations at OC-ALC include lime treatment and pressure filtration of a third of IWTP #11 (60 tons per month) and produce a filter cake of 32 percent solids that is subsequently dried to 70 percent solids (30 percent moisture). The current pressure filtration operation is limited by the blinding of the filter cloths that results in filtration times of about 290 minutes per run and frequent cleaning consuming 8 to 10 hours for every 4 or 5 runs.

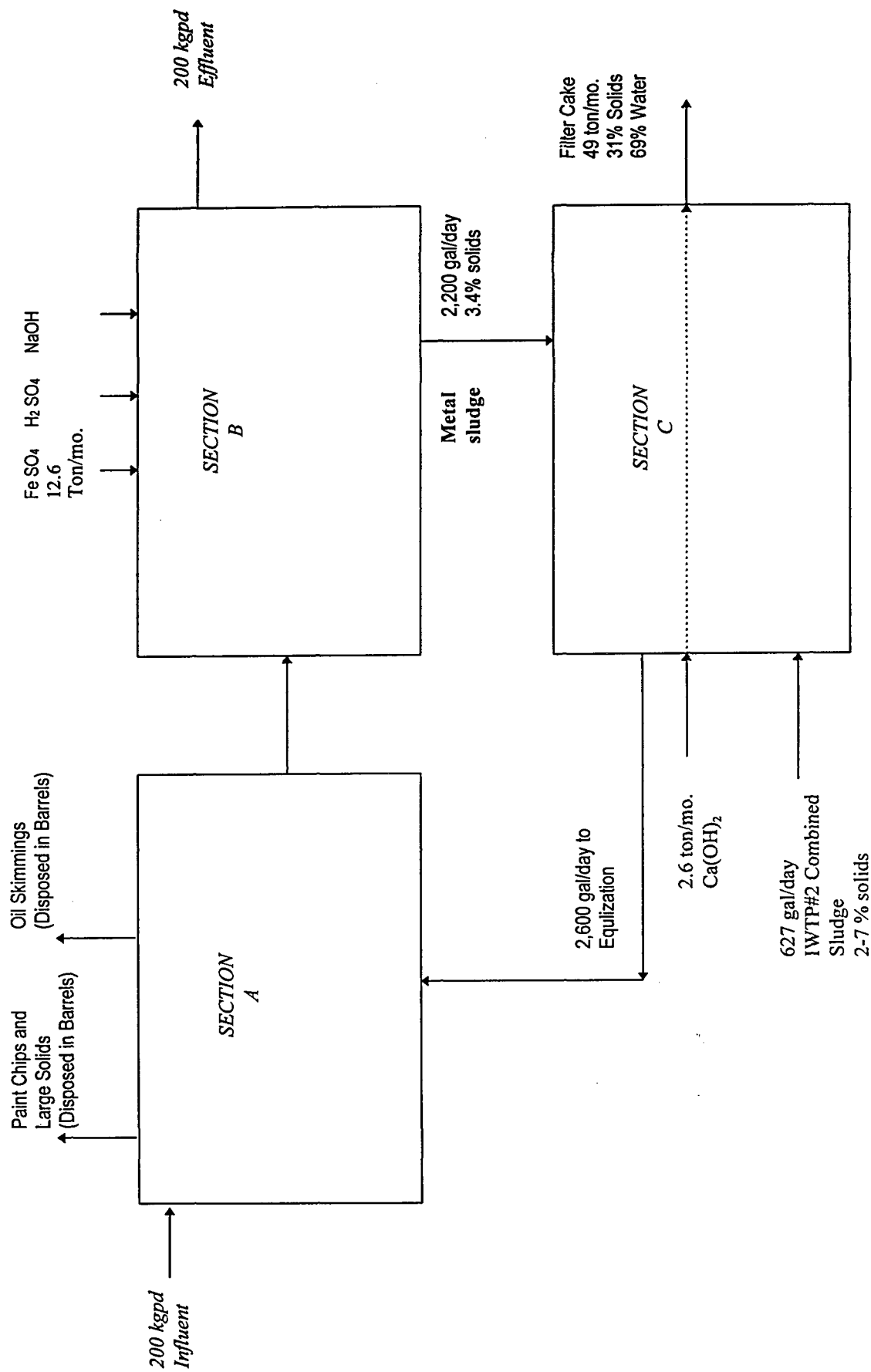


Figure 14. Block Process Flow Diagram of WR-ALC IWTP, Plant #1.

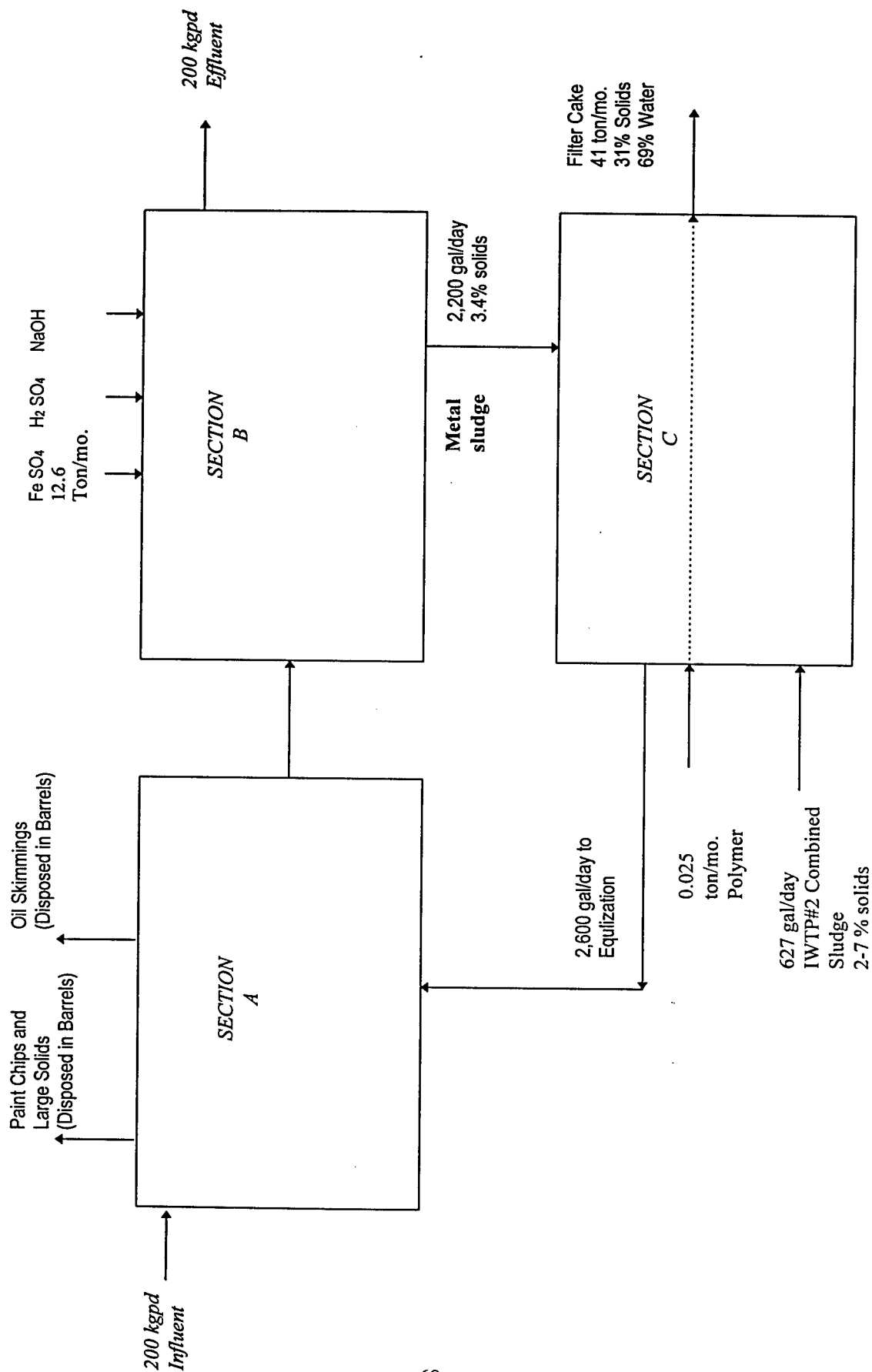


Figure 15. Effect of Proposed Flocculation Process on Process and Waste Streams at WR-ALC IWTP (Plant No. 1).

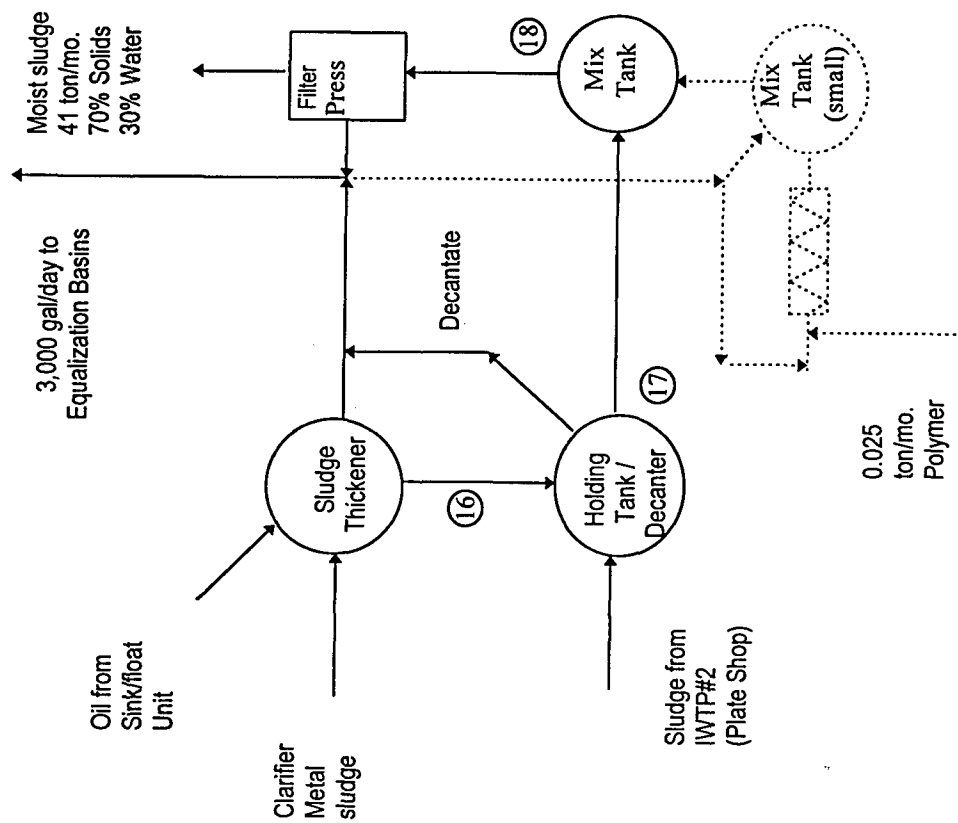


Figure 16. Proposed Equipment Changes for Flocculation of Combined Metal Sludges (IWTP #17) at WR-ALC IWTP .

TABLE 23. WASTE VOLUME REDUCTION BY PRESSURE FILTRATION OF FLOCCULATED OC-ALC IWTP #8 SLUDGE AND FERRIC CHLORIDE/LIME TREATMENT OF IWTP #10 SLUDGE.
(Basis: 100 Pounds of Thickened IWTP #11 Sludge at 10 % Solids)

		Current treatment of IWTP #11 filtered at 100 psi 290 min	Flocculation of IWTP #8 filtered at 100 psi 145 min	Lime treatment of IWTP #10, filtered at 100 psi 230 min
Solids content		32 % ^(a)	29%	33%
Additive		Ferric chloride and Lime	Flocculant	Ferric chloride and Lime
Additive quantity added, lbs		3.3	0.01	3.7
Without drying^(a)	Final waste quantity, lbs	87.6 ^(a)	23.0	21.2
			Total = 44.2	
	Waste quantity reduction compared to current treatment, %	Base Case	49.5	
With drying^(b)	Final waste quantity, lbs	77.8 ^(a)	9.5 ^(b)	10.0 ^(b)
			Total = 19.5	
	Waste quantity reduction compared to current treatment, %	Base Case	75.0	

^(a) Only a third of sludge is currently dewatered and dried.

^(b) All of the sludge is dewatered and dried.

In the proposed process the use of a precoat in the pressure filtration of flocculated sludge IWTP #8 (two thirds of the solids in IWTP #11 sludge) is expected to achieve a high solids content of up to 29 percent in the filter cake with only half the filtration time of IWTP #11. By employing the ferric chloride and lime treatment on biosludge (IWTP #10) alone, the use of ferric chloride and lime used per pound of sludge treated is reduced by 47 percent and the final solids content in the filter cake for the biosludge is increased to 33 percent. Furthermore, the separate ferric chloride and lime treatment of IWTP #10 precoat for the filtration of

flocculated IWTP #8 is expected to reduce filter cloth blinding. Thus, the capacity of the filter press may be increased by shortening of filtration runs and by shortening the frequency of filter cloth cleaning. Assuming that the original specification of the drier at OC-ALC was for the full filter press capacity, all the filter cake it produces may be dried to 70 percent solids. The block flow diagrams for the current process and the proposed process are shown in Figures 17 and 18, respectively. The equipment changes (additions) necessary to implement the proposed process are shown in Figure 19.

9. Economic Evaluation of Dewatering Options

An estimate of the economic potential of the proposed dewatering options was made for the WR-ALC and OC-ALC IWTP sludges. The procedure for economic analysis was as follows:

- (1) The purchased equipment cost (PEC) of equipment to be purchased was estimated using standard cost estimation procedures⁽²⁴⁻²⁶⁾.
- (2) The installed equipment cost, fixed capital investment (FCI) was estimated by applying a factor to PEC^(25,26).
- (3) The incremental chemical, labor, and utility costs were estimated.
- (4) The costs for maintenance, supervision, laboratory use, and plant overheads were taken as fixed percentages of the labor cost^(25,26).
- (5) Based on the net cost savings from a reduction in quantity of sludge disposed and an increase in operating cost for new equipment, a simple payback calculation was made^(25,26).

a. WR-ALC Option

This option consists of eliminating the use of lime by installing a flocculation system (see Figures 15 and 16). The cost of labor involved in operating the flocculation system is

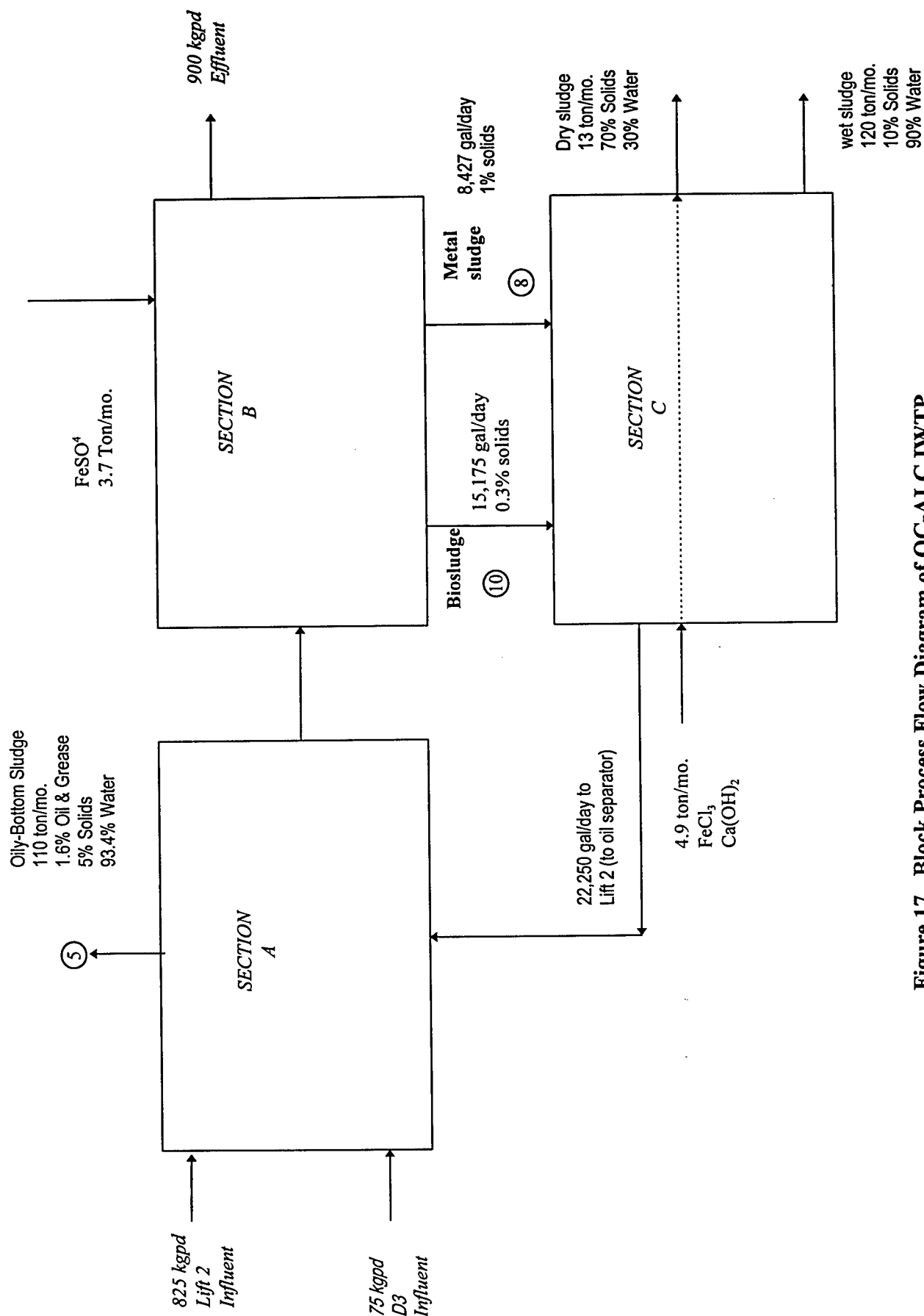


Figure 17. Block Process Flow Diagram of OC-ALC IWTP.

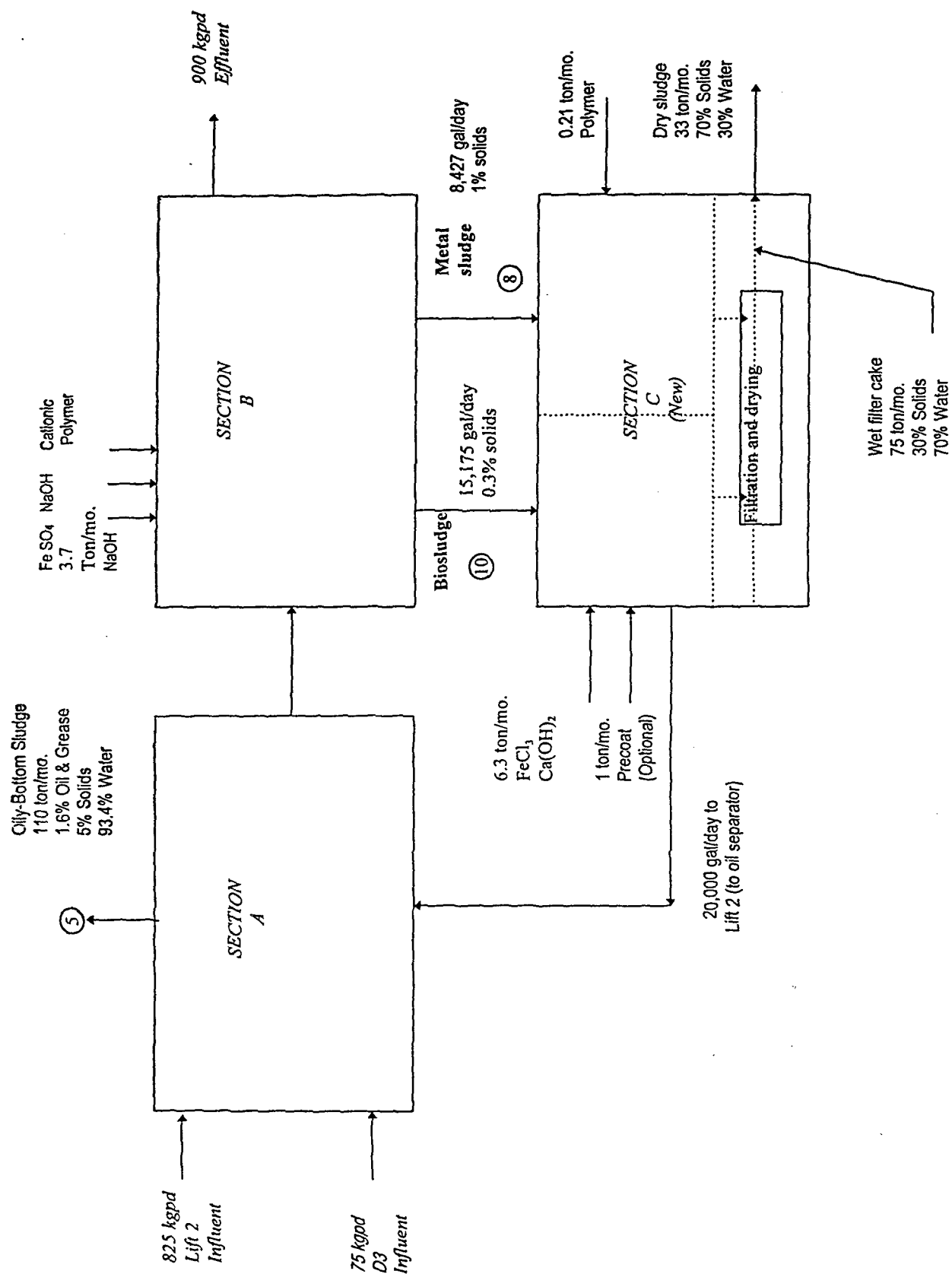


Figure 18. Effect of Proposed, Separate Treatment of the Metal Hydroxide and Waste Activated Sludges on Process and Waste Streams at OC-ALC IWTP.

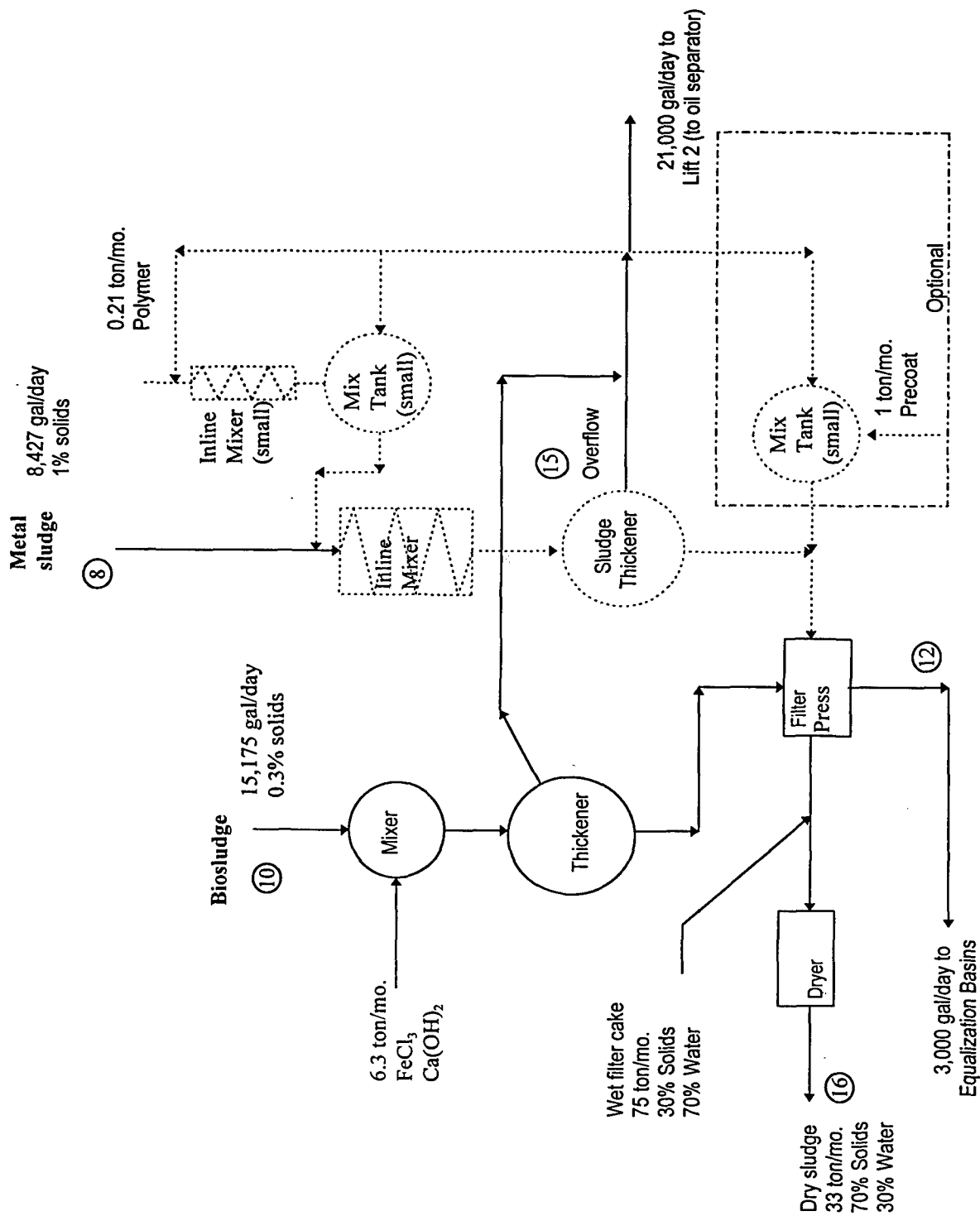


Figure 19. Proposed Equipment Changes for Separate Treatment of IWTP #8 and IWTP #10 Sludges at OC-ALC IWTP.

estimated to be the same as for the current lime treatment of sludge. A summary of economic analysis for this option is given in Table 24. The sludge quantity can be reduced by 16 percent (i.e., by 92 tons/yr) with a net annual savings of \$31,700. The simple payback period is estimated to be 2.0 years. Moreover, since lime addition is a manual operation, the proposed process is expected to be more acceptable to the IWTP operators.

b. OC-ALC Option

Treatment of OC-ALC sludge IWTP #8 by flocculation and IWTP #10 by ferric chloride and lime require the use of existing equipment to thicken IWTP #10 and apply the ferric chloride and lime treatment and the addition of a settling tank and polymer application system for IWTP #8 settling and flocculation (see Figures 18 and 19). The process economics are summarized in Table 25. The calculation of required filter press capacity using the current filter press (113 plates, 1200 mm square) results in 4 cycles per week (48 weeks per year) based on the solids content achieved using the lab press. The capital cost requirements are as follows: (a) an additional thickener with a 1-day holding time for IWTP #8 and a polymer addition system with an inline mixer^(6,12,26). Total capital expenditure on an installed cost basis is \$222,700. Payback based on the cost savings for dried sludge using the current drier is 0.5 years. If a 6,000-10,000 gallon, 9 foot tall tank is available for the thickening of IWTP #8, retrofitting it with a rotating sludge collector may reduce capital cost further. The application of the ferric chloride and the lime to IWTP #10 must be done in line at the inlet to the thickener, otherwise the biosludge will not settle.

The mixed sludge quantity may be reduced by 75 percent from 1600 tons/year to 391 tons/year if the current dryer is fully utilized as assumed above. If, however, the dryer is utilized at the current level, 680 tons/year of waste remains. The savings are then reduced from \$450,300 per year to \$364,400 per year and the payback period rises to 0.6 years.

**TABLE 24. ECONOMIC ANALYSIS OF PROPOSED FLOCCULATION/
DEWATERING PROCESS FOR WR-ALC IWTP #17 SLUDGE.**

Treatment Method,		Cr reduction	Current		
		Metal removal	Current		
		Sludge treatment	Flocculation		
Operating Schedule		Hrs/year	1,920	Electricity, cent/kWh	3.785
Hrs/shift	8	Shifts/day	1	Waste disposal cost, \$/lb	0.22
Days/week	5	Reduction of Sludge Quantity		92	ton/year
Weeks/year	48	for Disposal		16	Percent
PLANT CAPACITY		Flow rate, gal/day			280,000
CAPITAL COST					
Purchased Equipment Cost (PEC)					\$ 23,000
	Basis	Percentage			
Installation	PEC	40%			\$ 9,200
Instrumentation	PEC	20%			\$ 4,600
Piping	PEC	25%			\$ 5,750
Electrical	PEC	15%			\$ 3,450
Engineering	PEC	30%			\$ 6,900
Contingency	PEC	50%			\$ 11,500
Fixed Capital Investment (FCI) \$ (1996, installed)					\$ 64,400
OPERATING COST, \$/yr					
Materials					\$ 1,831
Maintenance, , 6% of FCI					\$ 3,864
Operating Supplies, 15% of maintenance					\$ 580
Electricity					
Operating labor			Current	\$ -	
Supervision,			Current	\$ -	
Laboratory charges,			Current	\$ -	
Plant overhead costs, 60% of labor +supervision +maintenance					\$ 2,318
Total operating cost					\$ 8,593
COST SAVINGS, \$/yr					
Savings in waste disposal cost					\$ 40,338
Net cost savings					\$ 31,745
PAYBACK PERIOD, yr					2.0

**TABLE 25. ECONOMIC ANALYSIS OF TREATMENT/DEWATERING
PROCESS FOR OC-ALC IWTP #8 AND IWTP #10 SLUDGES.**

Treatment Method,	Cr reduction	Current
	Metal removal	Current
	Sludge treatment	Flocculation
Operating Schedule	Hrs/year 5,760	Electricity, cent/kWh 3.785
Hrs/day/shift 8	Shift/day 3	Waste disposal cost, \$/lb 0.14 dry / 0.18 wet
Days/week 5	Reduction of Sludge Quantity 1,209 ton/year	
Weeks/year 48	for Disposal 75 Percent	
PLANT CAPACITY	Flowrate, gal/day	19,709
CAPITAL COST		
Purchased Equipment Cost (PEC)		\$ 79,520
	Basis	Percentage
Installation	PEC	40% \$ 31,808
Instrumentation	PEC	20% \$ 15,904
Piping	PEC	25% \$ 19,880
Electrical	PEC	15% \$ 11,928
Engineering	PEC	30% \$ 23,856
Contingency	PEC	50% \$ 39,760
Fixed Capital Investment (FCI)	\$ (1996, installed)	\$ 222,656
OPERATING COST, \$/yr		
	Basis	Percentage
Materials		\$ 4,789
Maintenance,	FCI	6% \$ 13,359
Operating Supplies	maintenance	15% \$ 2,004
Electricity		
Operating labor		\$ 14,400
Supervision,	labor	20% \$ 2,880
Laboratory charges,	labor	15% \$ 2,160
Plant overhead costs	labor +supervision	60% \$ 18,384
	+maintenance	
Total operating cost		\$ 57,976
COST SAVINGS, \$/yr		
Savings in waste disposal cost		\$ 508,241
Net cost savings		\$ 450,265
PAYBACK PERIOD, yr		0.5

10. Summary of Flocculation and Pressure Filtration Technology Evaluation

Treatment of WR-ALC metal hydroxide IWTP #17 sludge by flocculation followed by pressure filtration (without precoat) has an estimated payback of 2.0 years, requiring only the installation of a polymer mixing system. The proposed process can reduce the sludge quantity by 16 percent (92 tons/year). The current WR-ALC IWTP upgrade plans call for separating IWTP #2 sludge from IWTP #16 sludge. The results from laboratory testing show that IWTP #2 sludge can be treated by flocculation with a number of polymers, with Percol 727 and Cytec 1820 being preferred.

Pressure filtration may be combined with flocculation, the use of a precoat and different treatment strategies to dewater sludges at OC-ALC. Treatment of OC-ALC mixed, IWTP #11 sludge by use of flocculants reduced the specific cake resistance, but produced a semisolid filter cake which was difficult to handle. The strategy proposed is the separation of the two waste streams, namely IWTP #10 and IWTP #8. The waste activated sludge (IWTP #10) may be treated by addition of ferric chloride and lime followed by gravity thickening and pressure filtration. And the metal hydroxide sludge (IWTP #8) may be thickened and then treated with a flocculant followed by pressure filtration using a filter precoat. The proposed process can reduce the sludge quantity by 75 percent (1200 tons/year) assuming that the current dryer can operate at design capacity. The payback period for this option is only 0.5 years.

The enhanced dewatering tests recommended for pilot-scale evaluation are separate treatment of OC-ALC IWTP #8 and IWTP #10 sludges, and the flocculation of WR-ALC sludge IWTP #17. The flocculants recommended for OC-ALC IWTP #8 are Cytec 837 and Calgon Pol-E-Z-692. The flocculation of WR-ALC IWTP #17 sludge may be performed with Percol 727 and WR-ALC IWTP #2 sludge may be flocculated with either Percol 727 or Cytec 1820.

C. DRYING

1. Introduction

Because disposal costs are directly proportional to quantity (volume or mass), the majority of sludge disposal costs are due to the high water content of the sludge. Thus, dewatering and drying techniques to remove excess water would greatly reduce the quantity, and thus the cost, of sludge disposal^(6,12)

In order to justify investment in dewatering technology, removal of water from the sludge must be economical when compared with the current cost of sludge disposal as hazardous waste. To minimize the quantity of sludge that must be disposed as hazardous waste without expending unnecessary energy to remove all water, a target final solids content of the sludge for disposal is 70 percent. Several thermal drying methods, some in conjunction with mechanical dewatering techniques, were evaluated for their suitability to dewater the sludge to 70 percent solids. Thermal drying technologies, widely used in a variety of industries, include spray drying, fluid bed drying, and flash drying. An innovative thermal technique that has been used to dry various streams including sludges is pulse drying. Another innovative technique, developed by JWI, uses low humidity air to dry the sludge in a closed air loop. Mechanical dewatering techniques such as filter pressing or centrifugation may be used as a preliminary step before thermal drying. This combination optimizes dewatering efficiency while minimizing the costs of heat and energy required for the thermal methods. Since all AF-ALC IWTPs currently use filter presses, the thermal drying target was to increase the solids content from about 30 percent to 70 percent, which corresponds to 60 percent reduction in quantity of sludge disposed.

The characteristics of individual sludge streams play a large role in determining which dewatering technologies are appropriate. Bench scale testing on sludge streams is required to evaluate the suitability of each technology.

2. Various Types of Thermal Dryers

There are many types of commercial dryers. The dryers can be classified by the material they dry, the heating method, and whether the process is continuous or batch. The types of materials consist of rigid or granular solids, paste (semisolid), slurry, or liquid solution. The solids can be agitated during drying to increase the drying rate or to promote product characteristics. The heating method can be by direct contact or by indirect contact. Direct contact dryers use hot gasses or other means (i.e. microwave, infrared) to heat the material to be dried directly. Indirect dryers transfer the energy for drying through a solid media to the material being dried. For waste sludge drying, direct and indirect dryers are used depending in the solids handling characteristics of the sludge. If the sludge contains high amounts of volatile compounds that would be released during drying, either low temperature drying is used or a capture and control system is used to deal with the gaseous emissions generated during drying.

JWI supplies a batch dryer that uses low humidity air to dry the sludge in a closed air loop. The heat generated from the refrigeration unit is used to warm the air after the moisture has been condensed on cooling coils. Denver Sala, Fenton Environmental Technology, Inc., and Stord, Inc. use heated augers or rotating discs to dry sludge. The augers/discs increase the heat transfer area and provide the method to move the sludge through the dryer on a continuous basis. When needed the Denver Sala Holo-Flite® dryer and the Stord, Inc. Rotodisc® dryers can be covered by a hood to collect gaseous emissions generated during drying. The Fenton SludgeMASTER® includes a closed loop system.

Direct dryers are also used for sludge drying. JWI has dryers that use a moving belt/grate to move the sludge through the dryer and expose the sludge to hot combustion gasses or other heat source, such as infrared heaters. These direct heated dryers, currently used at OO-ALC and WR-ALC, are good for sludge containing low levels of oil and organic materials that would generate volatile organic compounds (VOCs) during drying.

Thermal dryers such as spray dryers, fluid-bed dryers, flash dryers, and pulse-combustion dryers are currently not used to dry sludges from small IWTP operations.

When sludge is not dry (solid) enough to be fed to a dryer, dried sludge can be recycled to the dryer inlet to produce a sludge consistency needed for dryer operation. This can be done on many of the continuous dryers.

3. Technical Challenges with AF-ALC IWTP Sludges

The water content in the sludge streams (before the filter press) was generally very high, with typical values at 10 percent or less solids, and measurements as low as 6.5 percent solids. Typical throughputs at AF-ALC IWTPs (e.g., at OC-ALC IWTP) are about 4 tons per day of wet sludge produced. At this throughput level, about 300 lbs/hr of water must be evaporated to achieve 70 percent solids content in the output stream.

There are several potential problems with using thermal drying techniques for dewatering sludges. Specifically, sludges with a significant oily content may tend to clog up drying apparatus, and will not dry fully. Oily sludges can also be problematic from a handling perspective. Another potential problem is the dust created during thermal drying. Analysis of sludge samples from OC-ALC (stream #11, mixed sludge, pre-filter press) indicates that virtually all of the solid particles are 40 μm or less in size, with most under 10 μm . To be "dustless," particles must be over 100 μm . An added concern is the solids composition, which consists primarily of metal oxides such as iron oxide, with trace amounts of metals such as chromium, lead, and nickel. Furthermore, there are some volatile organic constituents of these sludges specially at OO-ALC and OC-ALC, which could result in potential emissions; however, this problem is avoided in the JWI system. Finally, the sulfur and chlorine content of the sludges may result in the formation of SO_2 , HCl , and other chlorinated compounds during heating.

4. Test Facilities and Procedures

A number of vendors were contacted to determine the feasibility of various processes for drying the metal hydroxide sludges. In addition, a limited amount of sample and pilot scale analyses were conducted by vendors. A pilot test of the JWI low-humidity, closed-loop dryer, was conducted by OO-ALC and Battelle at an Army facility. Niro, Inc. (Columbia, MD.) Conducted a preliminary feasibility study of one sludge stream (OC-ALC IWTP #11). They

evaluated its potential for spray drying, fluid bed drying, and flash drying. Further evaluation of the post-filter press stream (OC-ALC IWTP #12) is being conducted by NIRO and Barr-Rosin to determine the feasibility of flash drying. Evaluation of OC-ALC IWTP #5 (oily sludge) is being conducted by Remediation Projects to investigate the feasibility of pulse drying. The heated auger or rotating disc dryers represent a potentially feasible option for AF-ALCs, but were not experimentally evaluated due to a lack of budget.

5. Results of Drying Tests

The pilot-scale tests on the JWI dryer were successfully completed as discussed later in this subsection.

Four other technologies, namely flash drying, spray drying, fluid bed drying, and pulse combustion drying, are still being evaluated by vendors. Based on an initial review of these technologies, however, it appears that the capital costs will be high because these will likely require some sort of emission control for particulates (PM-10) and possibly also for VOCs. Each drying system will likely produce different emission characteristics, depending on the exhaust air flowrate, system temperature, and entrainment. Based on the compositions of the sludges (primarily streams OC-ALC IWTP #11 and #5), a conservative estimate of the VOC emission rate is 28 lbs/hr (based on 4 tons/day wet sludge throughput, assuming a continuous operation) or 122 tons/yr. Uncontrolled dust emissions are similarly difficult to predict. Based on a mass balance and assuming a very conservative entrainment rate of 50 percent, about 16 lbs/hr particulates (uncontrolled) are estimated to be emitted (based on 4 tons/day wet sludge throughput). These drying technologies are discussed in more detail in Appendix E.

a. Demonstration of the JWI Low-Humidity Dryer

Tests were conducted at Toole Army Depot to determine the effectiveness of the low humidity, closed-loop dryer for drying IWTP sludge from OO-ALC.

(1) *Current Drying Operation at OO-ALC.* The OO-ALC industrial waste water treatment plant sludge before filtering are 5 to 10 percent solids by weight. After filtering the sludge contains from 20 to 40 percent solids depending on filter blowdown time. The sludge is currently dried before disposal as hazardous waste, using two gas fired JWI Model 360 dryers. The sludge generates dust and organic vapors during drying. OO-ALC currently uses an exhaust system that uses HEPA filters to reduce the opacity of the exhaust stream. Operators must be trained annually and the HEPA filters changed several times a year.

(2) *Pilot-Test.* Testing was performed using an older model (J-210, Oct. 93) of the JWI dry air dryer at Toole Army Depot (TAD). The dryer uses carts that are placed into the dryer cabinet for drying. The carts are placed under the filter press to collect the cake when the filter press is opened. The cart with the cake is then placed into the cabinet. The dryer, shown schematically in Figure 20, uses a dehumidifier to reduce the moisture content of the air circulated in the dryer to dry the filter cake. The dehumidifier coils cool the air to condense the water removed from the filter cake. The heat generated from the refrigeration system is then used to re-warm the air for continued drying. The dryer system is a closed air loop system, reusing the same air over and over again. The air moves up through the filter cake. The cart has louvers in the bottom to let air into the cart. The blower discharge is directed to the bottom of the cart with ducting that mates up to the bottom of the cart.

The test was conducted by borrowing a cart from TAD. Filter cake from the filter press at OO-ALC was placed into the cart. Half of the press, i.e., 17 of 39 plates, was placed into the cart. The cart was then be transferred to TAD for drying. The solids content of the sludge before drying were: 40.4, 34.3, 40.2, 36.0, and 36.1 percent solids (average value = 37.4 percent). The drying rate was determined by monitoring the rate of moisture condensation from the air. The condensed water was collected and measured in a graduated cylinder. The drying test was conducted over 12 hours. This was the usual drying time used for the sludge at TAD.

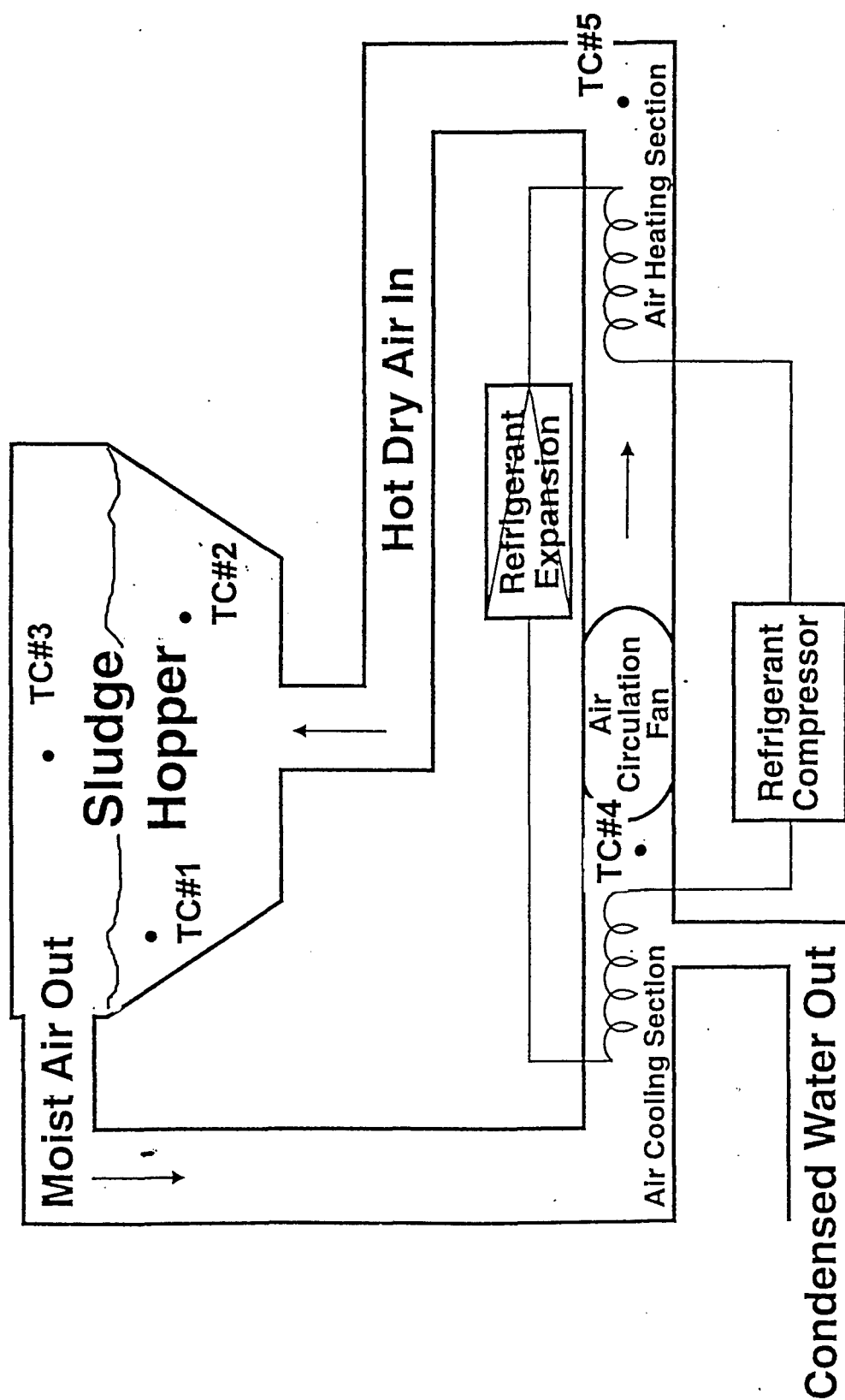


Figure 20. JW1 Batch Low Temperature Sludge Dryer.

Temperatures in the dryer were monitored by placing thermocouples into the dryer and cake to monitor and record temperatures over time. This information was not critical but was helpful in understanding what happened during drying. The temperatures that were recorded included the cake temperature, the warmed air temperature, and the chilled air temperature. A cake temperature rise indicated a change in the drying rate.

Power usage was estimated by the power requirement plate on the equipment. The plate stated 480 volts, 25 amps and three phase. The cost of electric power at OO-ALC is \$0.03 per Kwh. The cost to run the dryer for 12 hours is \$7.50. An estimate of labor was determined from the testing and interviews with staff at TAD who operate the dryer. The labor is less than one hour per batch drying. The time is needed for moving the cart and emptying the cart after the sludge is dried.

Any changes in the cake size and characteristics were observed and noted before and after drying.

Testing was carried out over two days. The first day involved placing OO-ALC sludge from the filter press in the waste water treatment plant into the drying cart. The filled cart was transported to TAD for testing. It was covered with a tarp during transport which took 1.5 hours. The cake settled from 2 to 4 inches during transport to TAD. The cart was placed into the dryer and the dryer was started. Data were taken during the first three hours of drying. The test data included the rate of water removed from the sludge and the temperature of the cake and the air drying the cake and is compiled in Table 26. A computer was used to record the temperature of the air above the cake overnight during drying.

TABLE 26. JWI LOW-HUMIDITY DRYER TEST DATA.
(Initial Weight of Sludge = 1430 lbs)

Time	Temperature (F)					Water Flow ^(a) (mL/min)
	TC#1	TC#2	TC#3	TC#4	TC#5	
1550	68	72	69	67	71	started test
1555	68	71	69	49	105	
1600	70	71	70	51	105	120
1605	72	72	72	53	109	286
1610	73	73	74	55	111	362
1615	74	74	75	56	112	
1620	75	75	75	56	111	380
1630	75	75	76	57	112	390
1640	76	76	77	57	113	410
1650	76	76	78	57	112	405
1700	76	76	77	57	113	410
1715	77	76	77	58	114	410
1730	77	76	78	58	113	410
1745	77	76	78	58	116	410
1800	79	77	78	58	114	410
1900	102	77	78	58	116	418
0805	97	84	79	74	72	Unit had shut off, opened unit and removed cart
0910	87	73				After opening the unit

^(a) Total water collected was 580 pounds (262, 740 mL).

The thermocouple locations (Figure 20) were as follows: TC #1 - front left corner of filter cake, 12 inches from each wall, 10 inches into the cake; TC #2 - rear right corner of filter cake, 12 inches from each wall, 10 inches into the cake; TC #3 - air temperature above the center of the cake; TC #4 - air temperature out of condenser; and, TC #5 - air temperature to the cart for drying.

(3) **Pilot-Test Results.** The drying data show that the constant drying rate was achieved in less than one hour. From the data logged by the computer, it appears that the constant rate drying period was over in about six hours (after 39 gallons removed, 70 gallons total). This was when the air temperature above the cake started to rise.

Weights were taken before drying and after drying by driving the truck used for transporting the sludge across a scales. The following weights were taken:

Total weight with wet sludge, cart, 55 gallon drum: 7800 pounds

Total weight with dry sludge, cart, 55 gallon drum: 7220 pounds

Total weight of empty truck, first time: 5640 pounds

Total weight of empty truck, second time: 5580 pounds

Total weight of truck with empty cart: 6320 pounds

Estimated weight of 55 gallon drum with lid: 50 pounds.

From these weights the total wet sludge was 1430 pounds (7800- 6320-50). The weight of water removed from the wet sludge was 580 pounds (7800-7220). Using a solids content of 36 percent before drying, the solids content after drying was 60.6 percent. The extra handling of the sludge to get it into the cart for drying and the transport to TAD resulted in settling which would reduce the air flow through the filter cake. The results of the test were still very encouraging.

6. **Technoeconomic Evaluation of JWI, Low-Humidity Dryer.**

The current gas fired dryers at OO-ALC require an operator to be present at all times while in operation. The energy cost for the gas fired dryers was \$3,350 in 1995. The gas fired dryers require pollution control equipment to reduce the dust and vapors generated during drying. This results in HEPA filters being changed out four times in 1995 at \$998 each filter. This amounts to an annual cost of \$3,992. These costs and the operation labor and training for opacity reading would offset any increases in utility costs for the proposed JWI system, which is very simple to operate. The capital cost of the low humidity, JWI dryer is

\$44,000 which is significantly lower than the cost for continuous dryers which start at over \$80,000. The continuous dryers also have high maintenance costs due to moving parts and high operating temperatures. Using the current average solids content of the gas dryer (56 percent) and a projected solids content of the dry air dryer (80 percent), the quantity of sludge disposed can be reduced by 32 percent. This would pay back the cost of two JWI dryers in about one year. The economic analysis is summarized in Table 27^(25,26).

Based on these tests, it is recommended that a full-scale, low-humidity JWI dryer be installed at OO-ALC and its performance be documented. This JWI dryer could be a system of choice for future upgrades of the OC-ALC and WR-ALC IWTP systems. Since WR-ALC does not currently have a dryer, the solids content using the JWI system can be increased from 30 percent to 80 percent, leading to sludge weight reduction of 62 percent based on the weight of the filter press cake. This will lead to an estimated 3.2 year payback.

**TABLE 27. ECONOMIC EVALUATION OF JWL, LOW-HUMIDITY DRYER
FOR REPLACING EXISTING DRYER AT OO-ALC IWTP.**

Treatment Method,		Cr reduction	Current		
		Metal removal	Current		
		Sludge treatment	Drying		
Operating Schedule		Hrs/year	2,688	Electricity, cent/kWh	3.785
Hrs/shift	8	Shifts	1	Waste disposal cost, \$/lb	0.26
Days/week	7	Reduction of Sludge Quantity		41	ton/year
Weeks/year	48	for Disposal		32	Percent
PLANT CAPACITY		Flow rate, gal/day			168
CAPITAL COST					
Purchased Equipment Cost (PEC)					\$ 88,000
	Basis	Percentage			
Installation	PEC	10%			\$ 8,800
Instrumentation	Included in PEC			\$	-
Piping	PEC	2%			\$ 1,760
Electrical	PEC	10%			\$ 8,800
Engineering	PEC	5%			\$ 4,400
Contingency	PEC	5%			\$ 4,400
Fixed Capital Investment (FCI) \$ (1996, installed)					\$ 116,160
OPERATING COST, \$/yr					
	Basis	Percentage			
Materials					
Maintenance,	FCI	6%			\$ 6,970
Operating Supplies	maintenance	15%			\$ (2,947)
Electricity					\$ 1,901
Natural gas					\$ (3,350)
Operating labor					\$ (36,000)
Supervision,	labor	20%			\$ (7,200)
Laboratory charges,	labor	15%			\$ (5,400)
Plant overhead costs	labor +supervision	60%			\$ (21,738)
	+maintenance				
Total operating cost					\$ (67,764)
COST SAVINGS, \$/yr					
Savings in waste disposal cost					\$ 52,259
Net cost savings					\$ 120,023
PAYBACK PERIOD, yr					1.0

SECTION VI

LABORATORY TESTS ON METAL REDUCTION

A. SPECIFIC OBJECTIVE

The specific objective of the metal reduction effort was to identify and screen alternative chemistries for separating metals from the IWTP waste waters which could result in a significantly smaller quantity of metal-containing waste stream for disposal or allow metal recovery.

B. APPROACH

Alternative chemistries to be evaluated were selected by consideration of the following:

- Discharge level targets for the treated water
- Number of toxic metals involved
- Chemistries of each metal impurity involved at the IWTP feed water conditions, and at key points in the IWTP process
- Currently practiced technology
- Emerging technologies for metals removal from water
- Operability
- Potential for enhancement of metal concentrate value
- Cost.

A survey of metal removal technologies was performed which focused on vendors, industrial practice, the open literature, patents, internal Battelle experience, and science/engineering fundamentals. This approach takes advantage of improvements in the available technologies for IWTP operations, and maximizes the use of commercially available materials as much as possible.

Four approaches for laboratory testing were identified (Table 28). These approaches are listed in the order recommended based on the screening test results provided later in this Section.

TABLE 28. METAL REMOVAL TECHNOLOGIES IDENTIFIED FOR LABORATORY TESTING.

Concept No.	Metal Removal Chemistry	Impurity Targets	Description	Potential Benefits
1.	Mixing and Oil Skimming (MOS)	Broad Spectrum Metal Ion Removal	Continuous contacting of influent waters, esp. from the chrome sump with water immiscible liquid chelating extractant "oil" phase. This extractant is recovered by oil skimming, continually regenerated, and reused.	<ul style="list-style-type: none"> Recovers and concentrates impurities without need for ferric salt/lime and coagulant/flocculant. Concentrate potentially useful to secondary metals market Continuous process
2.	Liquid Ion Exchange	Hexavalent Chrome, Cr ^{VI}	Same as (1) except use of different extractant and phase ratio	<ul style="list-style-type: none"> Recover Cr^{VI} for re-use Avoids need for FeSO₄
3.	Optimized Precipitation Methods	Broad Spectrum Metal Ion Removal	Hydroxide precipitation with SCC and no ferric salt added, with buffer, optionally with polymeric and/or PO ₄ ³⁻ /CO ₃ ²⁻ precipitation	<ul style="list-style-type: none"> Provide low metal residual except for Cr^{III} Similar to current process
4.	Substoichiometric Use of Ferrous Sulfate	Hexavalent Chrome, Cr ^{VI}	Uses <i>biodegradable</i> , cheap organic to "finish" the Cr ^{IV} -Cr ^{III} conversion	Uses 1/3 of the normal amount of FeSO ₄

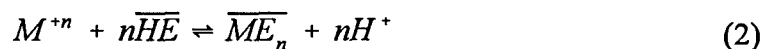
Screening tests were performed using synthetic IWTP feed streams. The best candidates from these tests were run against actual IWTP samples from OC-ALC. The results from these metal reduction screening tests are presented in this summary. Note that more description of the chemical speciation background chemistry for each approach was provided in the Tasks 1.1 and 1.2 Report⁽¹⁾, Section III.D., pp 42-60.

C. BROAD SPECTRUM TOXIC METAL ION REMOVAL BY MIXING/OIL SKIMMING (MOS)

1. Technical Description of MOS

The concept of broad spectrum removal of metal impurities by a special variation of oil skimming is based on the commercially well established, economical liquid-liquid extraction (LLX) technology used in the primary metals recovery industry, especially for metals such as Cu, V, U, and the rare earths. The concept is to convert LLX technology into a form familiar to IWTP operations: mixing followed by oil skimming or MOS.

The chemistry for broad spectrum metal removal from water using mixing/oil skimming can be generalized as,



The overbar illustrates a water immiscible "oil" phase of low viscosity, but high flash point (for safety). "HE" represents a weak acid, oil soluble, water insoluble, metal chelating organic compound which reversibly binds to metals rendering them oil soluble. M^{+n} represents all cationic metal ions which enter the IWTP with the feed water, such as Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} or Cr^{3+} .

The selection of HE to dissolve in the oil phase is set by the criteria given in Section VI.B. Suitable candidates for broad spectrum metal removal are given in Table 29.

**TABLE 29. BROAD SPECTRUM METAL
EXTRACTANTS TESTED.**

Extractant (HE)	Chemical Type	Chemical Supplier
LIX® 54	β-Diketone	Henkel-America, Tuc
LIX® 26 ^(a)	8-hydroxyquinoline	Henkel-America
NTHA-7 ^(a)	Hydroxamic acid	Met Tech Systems

(a) Developmental

These extractants bind cationic metal ions as per Reaction 2. To also recover anionic hexavalent chrome (CrO_4^-) along with the cationic metal contaminants, then Aliquat® 336 (or Alamine® 336) would also be blended into the extractant phase formulation (see Section VI.D.).

**TABLE 30. DESCRIPTION OF IWTP SAMPLES COLLECTED AT
OC-ALC USED FOR TOXIC METAL REMOVAL TESTING.**

Sample No.	Sample Description
46884-14-2	<p>Four gallon, 24 hour composite sample of oil skimmer aqueous waste stream from <u>chrome sump</u> stream (D3) collected from 11 a.m. 4/16/96 to 11 a.m. 4/17/96. Lot # ST2527-1030, Serial # P800244. Packaged into 4 1-gal positions.</p> <p>ICP analysis: Cu (23.6 ppb), Cr (9090 ppb), Pb (118 ppb), Cd (<7.1 ppb). pH = 8.27</p>
46884-14-27	<p>Four gallon, 24 hour composite sample of <u>equalization basin</u> overflow stream collected from about 12 p.m. 4/17/96 to 12 p.m. 12/18/96. Lot # ST25271030. Serial # P800253. Packaged into 4 1-gal positions.</p> <p>ICP analysis: Cu (<20.2 ppb), Cr (31.9 ppb), Pb (<7.3 ppb), Cd (<7.1 ppb), pH = 8.54</p>

2. Test Facilities and Procedures for MOS

Liquid-liquid extraction test procedures are standardized once an extractant system and associated chemistry are selected. These procedures, involving generation of samples for McCabe-Thiele plots were used to test the oil skimming (MOS) concept. For these tests, twenty percent solutions were prepared using the extractants from Table 29 and Aromatic 150 (75 percent) and Exxal® 10 (5.0 percent) (both of the latter from Exxon). Note that these components form a high flash point oil phase. The high flash point avoids flammability problems. This oil phase is referred to as the "extractant phase", E.

The synthetic IWTP aqueous feed solution containing a broad mixture of toxic metals (but no chromate(VI)) was prepared from the hydrated sulfate salts of Cu^{2+} , Cr^{3+} , and Cd^{2+} , and the soluble acetate salt of Pb^{2+} . All of these salts were of reagent grade purity. The water used was either DI water in the case of "synthetic" IWTP feed water, or the actual IWTP feed water sampled from the OC-ALC IWTP chrome sump or from the equilibrium basin (Table 30), as described in the text. The synthetic feed stream or "spiked" IWTP matrix feed were adjusted to add the impurity levels given by Table 31. These values were chosen based on analysis of data from various AF-ALC IWTP streams.^(1,2)

TABLE 31. SPIKED TOXIC METALS AND CONCENTRATIONS USED TO PREPARE BOTH SYNTHETIC AND ACTUAL IWTP FEED WATER.

Toxic Metal ^(a)	Concentration Target (ppb)	Form Used in Experiments	NPDES Limit (ppb)
Cu^{II}	2000	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	50
Cr^{III}	5000	$\text{Cr}_2(\text{SO}_4)_3$	100
Cr^{VI}	5000	$\text{K}_2\text{Cr}_2\text{O}_7$	100
Cd^{II}	2000	CdSO_4	20
Pb^{II}	2000	$\text{Pb}(\text{OH})_2$	100

(a) Two feed solutions were tested, as listed above but without the Cr^{VI} for an Equalization Basin sample, or only with Cr^{VI} for a D3 sample (Table 29).

Testing followed procedures similar to that given in Appendix E except that a pH

of 9.5 was used. The pH was adjusted using 1.0N NaOH.

3. Test Results for MOS Process

Tables 32 and 33 provide the MOS-LLX test results for the synthetic and actual IWTP feed water, respectively. For the synthetic feed tests, two mixing times and two E/A volume ratios were performed to allow realistic economics and residuals assessments.

TABLE 32. MIXING/OIL SKIMMING LLX TEST RESULTS WITH SYNTHETIC MIXED METAL FEED STREAM.

Extractant (A/E = 10:1)	Metal Concentrations (ppb)				pH
	Cd	Cr ^{III}	Cu	Pb	
Feed	2040	4500	2130	2100	3
NTHA-7	57	250	<3	<50	9.5
LIX-26	<1	120	4	<50	9.5
LIX-54	40	3	<3	<50	9.5
(A/E=100:1)					
Feed	2040	4500	2130	2100	3
NTHA-7	47	400	8	<50	9.5
LIX-26	<1	<9	<3	<50	9.5
LIX-54	5	15	<3	<50	9.5

The data in Table 32 are encouraging but only represent screening test results, and not an optimized process. For example, process development should include testing shorter mixing times and less efficient phase separation methods. Also, the variability in the Cr^{III} data, though small relative to the overall percent extraction of Cr^{III}, is understood to reflect the variability in mixing intensity (interface surface area) and/or exact pH adjustment procedure. Cr^{III} is sensitive to these parameters far more than the other metals because of its very slow rate of reaction with the chelating agent.

**TABLE 33. BROAD SPECTRUM METAL CONTAMINANT REMOVAL
FROM ACTUAL IWTP D3 STREAM USING MIXING/OIL
SKIMMING LLX.**

Feed: Cr Sump (D3) (Table 29) (0.2 μ filtered) Spiked as per Table 30.				
Extractant Phase:	20.0% NTHA-7® 5.00% Exxal 10® 75.00% Aromatic 150			
E/A = 0.100				
pH: feed = 8.27				
raffinate = 9.50-9.75 (adjusted and maintained with pH controller and 1.00 N NaOH Needed 18.2 μ l NaOH/cc feed only for first contact)				
t_{mix} : 120 seconds				
# Contacts: 3 (same aqueous, fresh E)				
Raffinate analysis (ppb):	Cd	Cr	Cu	Pb
Spiked Feed:	1650	13,700	1840	1590
Raffinate:	61	5570 ^(a)	<13	<1.2
D.L.:	13	36	13	1.2

(a) Residual Cr indicates presence as Cr^{VI}. This was confirmed by Cr^{VI} LIX experiments (see Section D).

4. Technical Evaluation of MOS Process

The general approach of using mixing/oil skimming (MOS) for removing toxic metals to dischargeable levels was generally found to be effective (Tables 32, 33). The pH 9-10 process condition matches the current IWTP process pH conditions for metals precipitation but MOS offers a much wider operating pH window (9-12 for MOS vs 9.0 ± 0.2 for metal hydroxide precipitation). Therefore, certain operational procedures would be similar to the current process but less strict.

Figure 21 provides the concept for inserting a MOS process in an IWTP. The flow rates are based on OC-ALC IWTP data and sulfuric acid is used for regenerating the extractant oil phase. Note that the IWTP feed water is only involved in one piece of equipment, the impurity extraction step. Because of the low E/A volume ratio of 1/10 to 1/100, the strip

equipment size will be about 1/10-1/100 the volume of the extraction equipment. Therefore, most of the capital cost will be in the extractor (see Section VI.D.5).

The advantages of the MOS-LLX process of Figure 21 are several,

1. Metals are substantially concentrated so that flocculation chemicals such as ferrous/ferric salts and lime are not needed (other than a very small, stoichiometric amount of ferrous sulfate needed for Cr^{VI} reduction as described in Section F).
2. Only the impurities are removed from the water (not the water from the impurities e.g., as is required for membrane processing or filtration, for example).
3. The metal concentrate could be precipitated and landfilled, as per current practice, or, since it has not been diluted with iron, calcium or sulfate, sent to the secondary recovery market so that its metal values, especially Cr (for stainless steel), can be claimed.
4. Low working capital inventory is provided by the continuous regeneration and reuse of the E oil phase.
5. High waste water flow rate is handled in only one mixer/settler unit per stage, minimizing equipment size and associated capital costs.
6. The process lends itself to continuous improvement. For example, the metals could eventually be recycled [see (3) above]. Another possibility is that the strip acid and strip base could be changed to phosphoric acid and ammonia, respectively, giving a filtrate from metal hydroxide/phosphate solids precipitation containing ammonium phosphate which can flow to the biotreatment plant as fertilizer/nutrients.

The economics of MOS-LLX relative to other options for metal reduction are discussed at the end of Section VI.

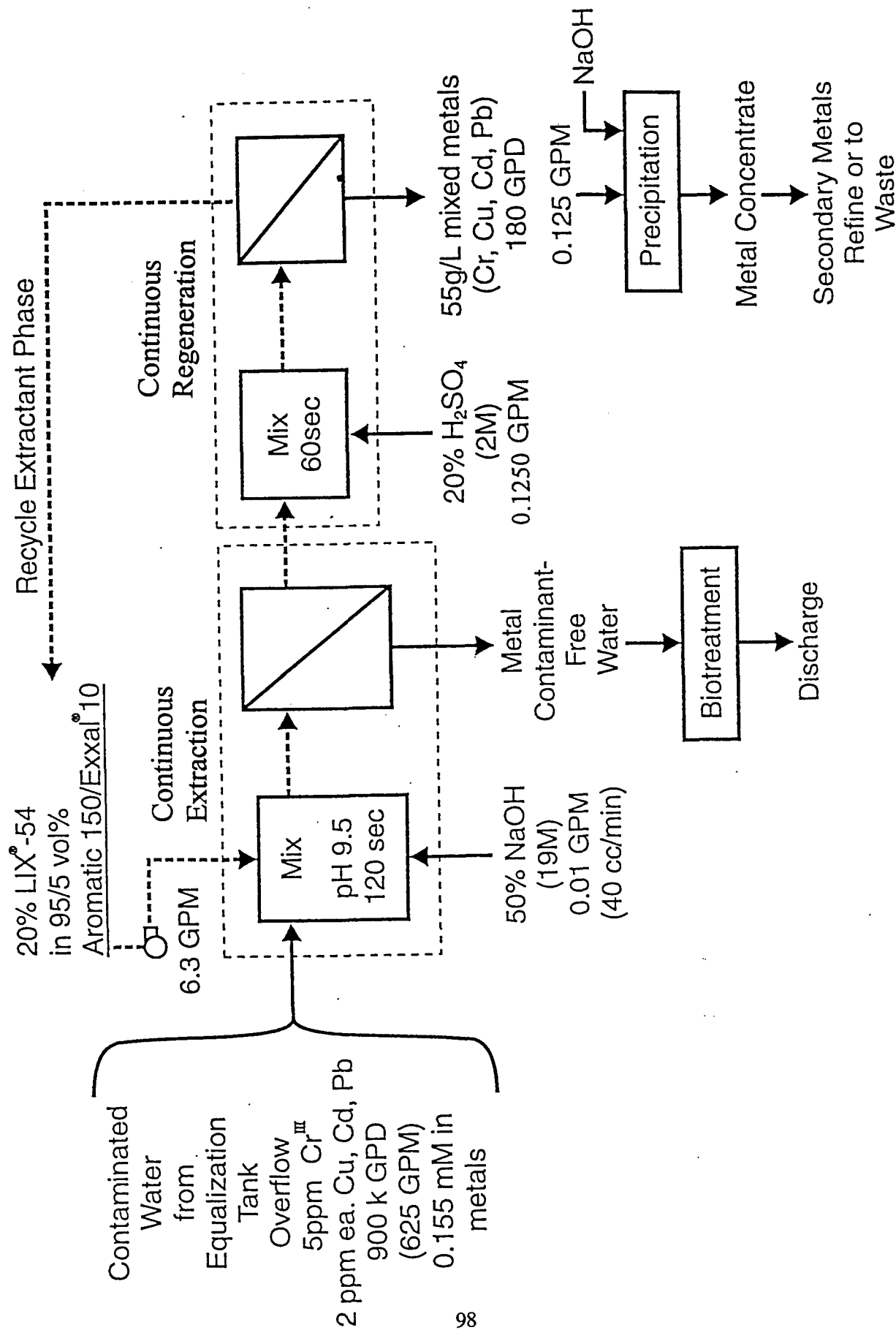


Figure 21. Process Concept for Inserting MOS-LLX in an IWTP for Removal of a Broad Spectrum of Toxic Metal Cations (Ref: OC-ALC IWTP).

D. HEXAVALENT CHROME REMOVAL BY ANION LIQUID ION EXCHANGE (A-LIX)

As in the case of MOS-LLX, anion liquid ion exchange (A-LIX) is used to extract ions in a liquid-liquid extraction device, the only difference being that in A-LIX, anions are extracted while in MOS-LLX, cations are extracted. The A-LIX was evaluated for extraction of Cr^{VI} to avoid using excessive amounts of ferrous sulfate.

The anion liquid ion exchange (A-LIX) offers several process advantages:

1. It can handle the high flow rates at the IWTP
2. It is continuous
3. It offers a range of chemistry and engineering variations which can provide economic and waste avoidance options
4. It is a proven technology for the large scale production of metals from ores by extractive hydrometallurgy
5. It can provide large reductions in waste stream flow with concomitant large concentration increases in the concentration of metal contaminant, even to the point of enabling recycling of such contaminants
6. It can handle low ppm metal concentration reductions to ppb levels.

1. Technical Description of A-LIX

a. Background for Hexavalent Chrome for Plating and Painting Operations

Alodine is used in both chrome plating and in the production of conversion coatings in painting operations. Alodine is a solution of mostly chromic oxide, CrO_3 , in water (where it forms chromic acid, H_2CrO_4), and a small amount of sulfuric acid. The oxidation state of the chromium in these solutions is hexavalent, i.e. Cr^{VI} , or chromium(VI). The specific chemical species in solution is discussed below.

As it is used in chrome metal plating, most of the chromium from the Alodine bath ends up on parts as chromium metal product. However, some of the Cr^{VI} is reduced to Cr^{III} by the metal substrate during the initial chrome metal layer formation while the metal surface is exposed and galvanic reactions can occur. Fortunately however, since the plating cell is

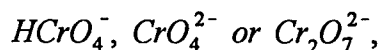
undivided, this Cr^{III} is re-oxidized at the anode back to Cr^{VI} , and so does not represent a loss of chromium raw material provided the anode surface area is sufficiently larger than the cathode's. These baths have a very long lifetime of about ten years. Therefore the only problem stream which exits in the chromium metal plating process is the rinse water which contains dilute Cr^{VI} . Also, in painting operations, the spent Alodine solution is soaked onto the parts and then rinsed off. This diluted rinse is not reusable and represents a discharge stream containing Cr^{VI} , at ca. 1-10 ppm (at the IWTP chrome sump discharge D3 Stream).

Therefore, from both the plating and the painting/conversion coating operations, the Cr^{VI} waste is a slightly acidic water solution containing 1-10 ppm Cr^{VI} . These Cr^{VI} levels are above NPDES discharge levels. The order of magnitude variation in concentration represents an additional constraint on any chromium removal process. Note (Table 30) that at least at OC-ALC IWTP, the pH of both the chrome sump D3 stream and the equalization basin are more nearly 8.3 due to other streams being mixed with the Cr^{VI} containing rinse waters.

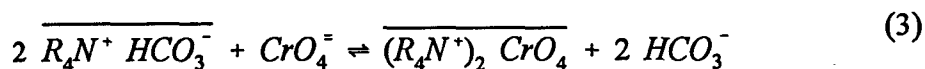
Minor amounts of Cr^{VI} also exit the plating process as solids. These are inadvertently produced at a very slow rate as the lead anodes slowly corrode, contributing lead ion to the bath, which then causes the precipitation of orange colored lead chromate, PbCrO_4 , sludge. This sludge accumulates on the bottom of the tank. Since it is difficult to filter, it is periodically cleaned out manually and to date hasn't represented an operations problem.

b. Liquid Ion Exchange for Hexavalent Chrome Removal from Water

Liquid Ion Exchange (LIX) is a form of Liquid-Liquid Extraction (LLX) wherein the extraction mechanism is by ion pairing. Chromate(VI) ion is anionic. We will use A-LIX to designate anion liquid-liquid extraction process. The anionic chromate(VI) chemical species present in water depending on pH and total Cr^{VI} concentration are,



Oil soluble, cationic amine extractants (R_4N^+ , R_3NA^+) are effective for the recovery of anions, especially chromate(VI), from water^(27,28). The extraction reaction written for the R_4N^+ case is (written for bicarbonate anion as the strip anion, which can be varied),

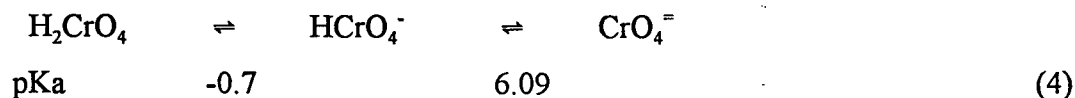


Stripping is achieved by reversing Reaction 3. This is done by washing the oil phase with strong caustic or salt solution such as Na_2CO_3 , $NaCl$, Na_2SO_4 , etc. Sulfuric acid also can be used, but is not as efficient. The use of sodium sulfate, sulfuric acid, or caustic has the advantage of providing a recyclable hexachrome concentrate which can be returned to the painting or plating operations. The amount of sodium ion present should be minor and is not expected to upset the process chemistry of these operations. This sodium would eventually exit the process via the raffinate.

Although Chromium(VI) is a strong oxidant at strongly acidic conditions, or in the presence of strong reducing agents (such as ferrous ion, reducing organics, or borohydride), chromate(VI) ion is fairly stable with respect to oxidation reactions at mild pH values, e.g. pH 3-4. Therefore at the conditions of the rinse waters, CrO_4^{2-} can behave as a stable anion.

c. pH Considerations

In highly dilute solution, such as are experienced at the IWTP, the dichromate(VI), $Cr_2O_7^{2-}$, species is not favored, therefore, the only Cr^{VI} species to consider are the following,



Although the CrO_4^{2-} dianion might be expected to be the most strongly extracted by anion liquid ion exchange, the difficulty in solvating the dianion in the nonpolar E phase makes the monoanion $HCrO_4^-$ easier to extract. Hence, for the most efficient Cr^{VI} removal A-LIX based process, the pH needs to be in the 1-5 range.

A second pH consideration involves the tertiary amine extractant which also involves protic equilibria. If present, this acid/base equilibria provides a "pH swing" basis for extraction and stripping. Representative pKa values for amines with varying degrees of alkyl substitution are given in Table 34.

TABLE 34. COMPARISON OF pKa VALUES FOR AMINE EXTRACTANTS⁽¹⁾

Quaternary Amine	Tertiary Amine	Secondary Amine	Primary Amine
R_4N^+	R_3NH^+	R_2NH^+	RNH_3^+
pKa ^(a) Strong Base	10.75	10.97	10.57

(a) Based on R=Et (or I - Pr for the monoamine), but applicable to R=alkyl.

These pKa values are close enough to each other to allow extractant selection to be based on operational criteria (e.g., phase separation rates, water carryover, degradation rates, etc.) On this basis the order of preference is:

tertiary amine > secondary amine > primary amine

Note that in the A-LIX operation the above ethyl groups would be substituted by octyl groups to render the extractant insoluble in water and soluble in oil. The effect of increasing the carbon number in this manner is that the extractant becomes water insoluble. Then for the R_4N^+ or R_3NH^+ species to exist in the E phase, the positive charge must be solvated. IDA provides this E phase solvation for the cationic amines. The net effect on R_3NH^+ , however, is that the PKa value is shifted to ~6-7. Therefore, the optimum pH range for A-LIX operations using R_3NH^+ extractant is also ~2-6. To maximize the concentration of recovered hexavalent chrome, tertiary amine is the extractant of choice.

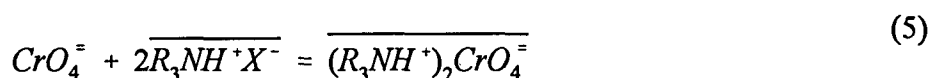
Quaternary amines, R_4N^+ , are a separate class of chemistries and must be tested separately. Quaternary amine extractants (e.g. Aliquat®336) on the other hand are not restricted by pKa limitations like other amines, and so would have a broad pH operating window, limited only by the pKa of $HCrO_4^-$. Therefore, the pH operating window for Aliquat®336 is ~1-6. Higher pH values, e.g., as high as ca. 9.0, could be used if a sufficient number of extraction stages are employed.

As the tertiary amine is a weak base, the pH of the extractor may rise. PH control in the extractor can be controlled using mineral acid.

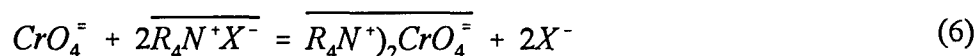
d. Extractant Selection

The two extraction reactions selected for testing were:

for Alamine®336 ($R_3NH^+X^-$),



for Aliquat® 336 ($R_4N^+X^-$),



Where X is chosen to provide the desired product form. For example X^+ can be HCO_3^- as shown in Reaction 3. The loading of X onto the extractant is accomplished during the stripping, "pre-equilibration" (if needed) or extraction steps as described below. Notice that the Cr^{VI} is not reduced to Cr^{III} in the extraction step and so chemicals normally added for Cr^{VI} reduction are not consumed in the LIX extraction operation.

The solvent for the extractant phase was Aromatic® 150 (Exxon), a 85 percent aromatic, high flash point solvent commonly used in solvent extraction hydrometallurgy to provide the physical, safety, and solubility characteristics needed for Aliquat® 336 or Alamine®

336. In addition five percent isodecanol (Exxal® 10, Exxon) was used as the "modifier" to help solubilize the extracted ion pairs and thereby prevent the formation of three phases.

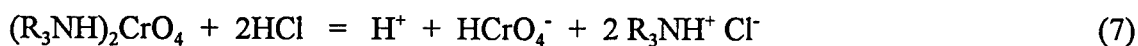
e. A-LIX Process Considerations

The A-LIX technology needs to be capable of removing 1-10 ppm Cr^{VI} from water down to ≤ 100 ppb, preferably in one contact, but at least after several stages of contact. The waste water could also be slightly acidic (as the plating and painting acids are also diluted), and may be expected to contain other contaminants from the painting operations. Both actual IWTP and a synthetic, solids free, feed solution were tested.

f. Cr^{VI} Stripping from the Extractant

Several Cr^{VI} stripping options exist: ion exchange; neutralization; and, reductive ion exchange. While these stripping options are established well enough in the literature to make it necessary to test these in the laboratory, these are described below.

(1) Ion Exchange Stripping. This strip method is just the reverse of reactions 5 and 6 above. For example, aqueous HCl could be used to strip the Cr^{VI} from the loaded Alamine® 336 phase by the following chemistry,

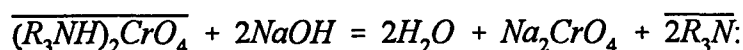


A similar reaction can be written for Aliquat® 336. The use of concentrated HCl, would allow the production of concentrated chromic acid. The corrosivity of HCl is an important issue that would need to be addressed unless it already has, as is the case in many plating shops. Other strip acids can be used as well, such as sulfuric and phosphoric. The value of using these acids is that the product chromic acid strip concentrate might be recycled directly back into the painting or plating operations.

It is not necessary to strip with acid. Sodium chloride, sodium sulfate, ammonium carbonate, ammonium chloride, ammonium sulfate, etc. are other options for

Cr stripping. The choice of strip agent depends upon process operability, cost, and the desired fate for the Cr^{VI} concentrate product.

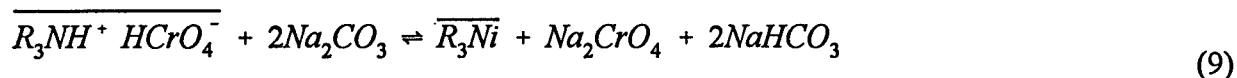
(2) *Neutralization Stripping.* For Alamine® 336 there is an additional very important stripping option, neutralization, as shown by the following reaction:



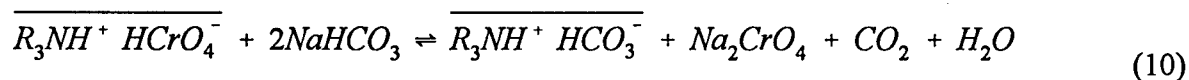
High concentration factor, for example several hundred fold, are possible with the neutralization option. In this case the extractant is converted into a neutral form which can no longer ion pair with the chromate(VI) ion, thereby forcing the chromium into the aqueous phase to maintain charge balance. The net result is a very high distribution coefficient, resulting in very high concentration factors. Potassium hydroxide and sodium carbonate are two other bases that can be used in place of NaOH. However, NaOH is already present in IWTP operations and, when neutralized, usually displays acceptable economics and environmental impact.

The drawback of using Alamine® 336 with neutralization stripping is that all of the amine needs to be neutralized to effect Cr^{VI} stripping, not just the portion ion paired with chromate(VI) ion as is the case for Aliquat®336. Therefore, the minimum concentration of extractant needed to provide sufficient Cr removal in the extraction step should be used. Optimizing Cr concentration volume ratios across the extraction/strip (E/S) circuit also reduces this neutralization cost as well as providing a low volume of Cr "product" concentrate which needs to be dealt with downstream. Lastly, the caustic strip solution is recycled internally so that it is fully spent by the time it leaves the circuit as a sodium chromate(VI) concentrate. A benefit in using sodium hydroxide (or potassium hydroxide) as the strip aqueous phase is that these chromate(VI) salts are commercially useful. Therefore, the chromate(VI) concentrate may be acceptable as a raw material for manufacturing chromate(VI) products, such as pigments, CrO₃, etc.

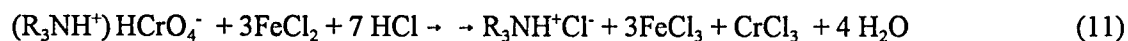
Neutralization stripping using soda ash is attractive from the viewpoints of mild reaction conditions and low raw material costs. However, its stripping reaction with Alamine®336 is unique (Reaction 9):



Therefore, sodium bicarbonate is a co-product from the stripping reaction. When the pH falls from about 12.2 to 10.33, 50 percent of the soda ash will have been consumed. When the pH falls to 8.5, 100 percent of the soda ash will have been converted to NaHCO₃. Note that NaHCO₃ will provide some stripping action by ion exchange according to Reaction 10, where CO₂ gas is released in proportion to the amount of Cr stripped.



(3) **Reductive Stripping.** In the reductive Cr stripping approach, the stripping thermodynamic driving force is the conversion of anionic chromate(VI), which has a high affinity for the extractant, to cationic chromium(III), which has no affinity for the cationic amine extractant. For example, slightly acidic ferrous sulfate would provide this chemical reduction activity according to Reaction 11:



Ferrous sulfate may be used in place of ferrous chloride. Other reducing agents may be acidic bisulfite/metabisulfite/SO₂, stannous chloride, etc. Sulfite may react slowly and so a counter-current continuous LIX system may need mixer compartments suitably heated and/or sized. Alkaline sodium borohydride would be another system viable at high (≥12) pH.

(4) *Fate of Recovered Chromium Concentrate.* A number of options exist for the disposal of the chromium concentrate (spent strip raffinate). For the case of reductive stripping, the stripped concentrate containing the reduced Cr in the Cr(III) oxidation state would be sent on with the rest of the IWTP process aqueous phase to metal hydroxide precipitation. Alternatively, the metals could be precipitated separately yielding a relatively pure Ferrochrome oxide which might be placed on the stainless steel raw materials market. Sodium chromate(VI) concentrate from caustic or soda ash stripping may be reusable in the painting alodine bath.

2. Test Facilities and Procedures for A-LIX

a. Facilities

Test facilities were the same as used for Section VI.

b. Raw Materials

Both synthetic and actual IWTP feed streams were tested (Tables 30 and 31). These solutions either contained 10 ppm of spiked Cr^{VI} (from K₂Cr₂O₇), or in the case of the actual IWTP solution, 10 ppm in addition to that already contained in the sample.

(1) *Synthetic Influent Feed Test Solution.* Based on the background information provided above, a reliable synthetic test solution for Cr^{VI} influent is 10 ppm Cr^{VI} in slightly acidic water. This solution was prepared from 1000 ppm stock AA standard potassium dichromate(VI) solution (Aldrich Chemical Company). This solution, diluted 100x with deionized water, was used as the synthetic influent water "feed" in the experiments described below.

(2) *LIX Extractant Phase Ingredients.* The LIX extractants, Alamine® 336 and Aliquat® 336, are Henkel America products with many decades of proven field experience in metals recovery. The modifier Exxal® 10 and the solvent Aromatic® 150 are Exxon products and are also proven reagents for amine based LIX systems from the extractive hydrometallurgical industry. These materials are of high flash point and are "nonflammable" by safety standards.

All other chemicals and reagents are commonly available in the laboratory and were of ACS reagent grade or better. Deionized water was used for preparation of solutions and dilution of analytical samples.

c. Analytical

Normal ICP was used for total Cr analytical method.

It was not necessary to analyze the extractant phase directly since the total Cr added in an extraction experiment (the "feed") was known, and since the extraction phase volumes are known. Therefore, the Cr levels on the extractant phase were reliably obtained by difference. Observance of any solids formation and interface conditions were made to eliminate the concern/possibility that Cr concentration reductions occurred by precipitation, by forming a third phase or a stable emulsion.

Samples were immediately acidified with a known volume of 6 percent nitric acid to insure adequate shelf life for the hold period prior to ICP analysis.

d. Experimental Procedures

The standard means of evaluating the LIX circuit at the laboratory, non-continuous scale is to perform tests to obtain phase equilibrium data, represented by McCabe-Thiele (M-T) plots. From one M-T chart, several design calculations can be made. The concept is tested for a particular extractant formulation, the number of extraction (or strip) stages needed is determined, as is the optimum E/A volume ratios, the expected residual Cr level left in the final process raffinate and the concentration enhancement expected. These M-T experiments are described below for the subject system.

The extractant was prepared by blending the above reagents and constituents and pre-equilibrating the mixture by stripping with HCl to load the exchangeable anion onto the extractant. Detailed experimental procedures are provided in Appendix C. Chromium extraction experiments were repeated for each sample listed in the test matrix (Tables 35 and Table 36).

**TABLE 35. EXPERIMENTAL TEST CONDITIONS FOR EVALUATION OF
LIX EXTRACTANT ALAMINE® 336 FOR Cr^{VI} REMOVAL.**

Sample Number	Prepared Volumes			Volume Ratios (Initial)
	V _A (mL)	V _E (mL)	V _{tot} (mL)	E/A
4752809-				
1-1	4.00	80.00	84.00	20.0
1-2	4.00	40.00	44.00	10.0
1-3	7.00	35.00	42.00	5.00
1-4	10.00	30.00	40.00	3.00
1-5	10.00	20.00	30.00	2.00
1-6	20.00	20.00	40.00	1.00
1-7	20.00	10.00	30.00	0.500
1-8	30.00	10.00	40.00	0.330
1-9	35.00	7.00	42.00	0.200
1-10	40.00	4.00	44.00	0.100
1-11	80.00	4.00	84.00	0.050
1-12	20.00	20.00	40.00	1.00

**TABLE 36. EXPERIMENTAL TEST CONDITIONS FOR EVALUATION OF
LIX EXTRACTANT ALIQUAT® 336 FOR Cr^{VI} REMOVAL.**

Sample Number	Prepared Volumes			Volume Ratios (Initial)
	V _A (mL)	V _E (mL)	V _{tot} (mL)	E/A
4752809-				
2-1	4.00	40.00	44.00	10.00
2-2	4.00	35.00	42.00	5.00
2-3	10.00	20.00	30.00	2.00
2-4	10.00	30.00	40.00	3.00
2-5	10.00	20.00	30.00	2.00
2-6	20.00	20.00	40.00	1.00
2-7	20.00	10.00	30.00	0.500
2-8	30.00	10.00	40.00	0.330
2-9	35.00	7.00	42.00	0.200
2-10	40.00	4.00	44.00	0.100
2-11	80.00	4.00	84.00	0.050
2-12	20.00	20.00	40.00	1.00

Strip experiments were not performed since this technology is already fairly well established.⁽²⁾ Strip optimization experiments should be performed prior to any pilot testing of the process.

3. Test Results for A-LIX

a. Synthetic IWTP Feed

The hexavalent chrome extraction results for Alamine® 336 and Aliquat® 336 are summarized in Table 37 and plotted in Figure 22 for the synthetic IWTP feed stream containing 10 ppm Cr^{VI}.

During the extraction experiments it was observed that the yellow color of the extractant phase turned a bright yellow in color as the E/A volume ratio decreased for both extractants using the synthetic feed. This result is consistent with yellow colored chromate(VI) ion, CrO₄⁼ being absorbed into the E phase without reduction to blue/green chromium(III) species. This result is as expected based on the Henkel product literature for these amine extractants.⁽¹⁾

b. Actual IWTP Feed

Table 38 summarizes hexavalent chrome A-LIX extraction results for both Alamine® 336 and Aliquat® 336 extractant systems using actual IWTP feed.

4. Technical Evaluation of A-LIX Process

Figure 22 illustrates that a high (~100 percent) recovery of hexavalent chrome is possible from synthetic IWTP feed using either Aliquat® 336 or Alamine® 336 at pH of 2-4, and that the percent removal is a strong function of E/A ratio. As expected, the lower the E/A, the lower the percent extraction per stage, but the greater the Cr^{VI} concentration achieved on the extractant phase. For 90 percent Cr^{VI} removal, E/A values of at least 0.4 and 0.2 are needed for Aliquat® 336 and Alamine® 336, respectively.

**TABLE 37. HEXAVALENT CHROME A-LIX REMOVAL RESULTS
FOR SYNTHETIC IWTP FEED CONTAINING 10 PPM Cr^{VI}.**

Sample Number	E/A	[Cr] _{eff}	q ^(a)	%E (Cr)
4752809				
20% Alamine® 336 (5% Exxal® 10, 75% Aromatic 150)				
1.1	20.00	0.260	37.5	99.9
1.2	10.00	0.540	17.5	99.4
1.3	5.00	0.290	33.5	99.4
1.4	3.00	0.710	13.1	97.5
1.5	2.00	0.140	70.4	99.3
1.6	1.00	0.240	40.7	97.6
1.7	0.50	0.280	34.7	94.6
1.8	0.33	0.310	31.3	91.2
1.9	0.20	0.510	18.6	78.8
1.10	0.10	0.370	26.0	72.2
1.11	0.05	1.170	7.55	27.4
1.12	1.00	0.340	28.4	96.6
20% Aliquat® 336 (5% Exxal® 10, 75% Aromatic 150)				
2.1	10.00	0.120	82.3	99.9
2.2	5.00	0.190	51.6	99.6
2.3	2.00	0.320	30.3	98.4
2.4	3.00	0.250	39.0	99.2
2.5	2.00	0.600	15.7	96.9
2.6	1.00	0.460	20.7	95.4
2.7	0.50	0.340	28.4	93.4
2.8	0.33	0.790	11.7	79.5
2.9	0.20	1.030	8.7	63.5
2.10	0.10	0.980	9.2	47.9
2.11	0.05	0.880	10.4	34.1
2.12	1.00	0.860	10.6	91.4

^(a) See footnote to Table 37 for definition of "q".

Anion Liquid Extraction of Cr(VI)

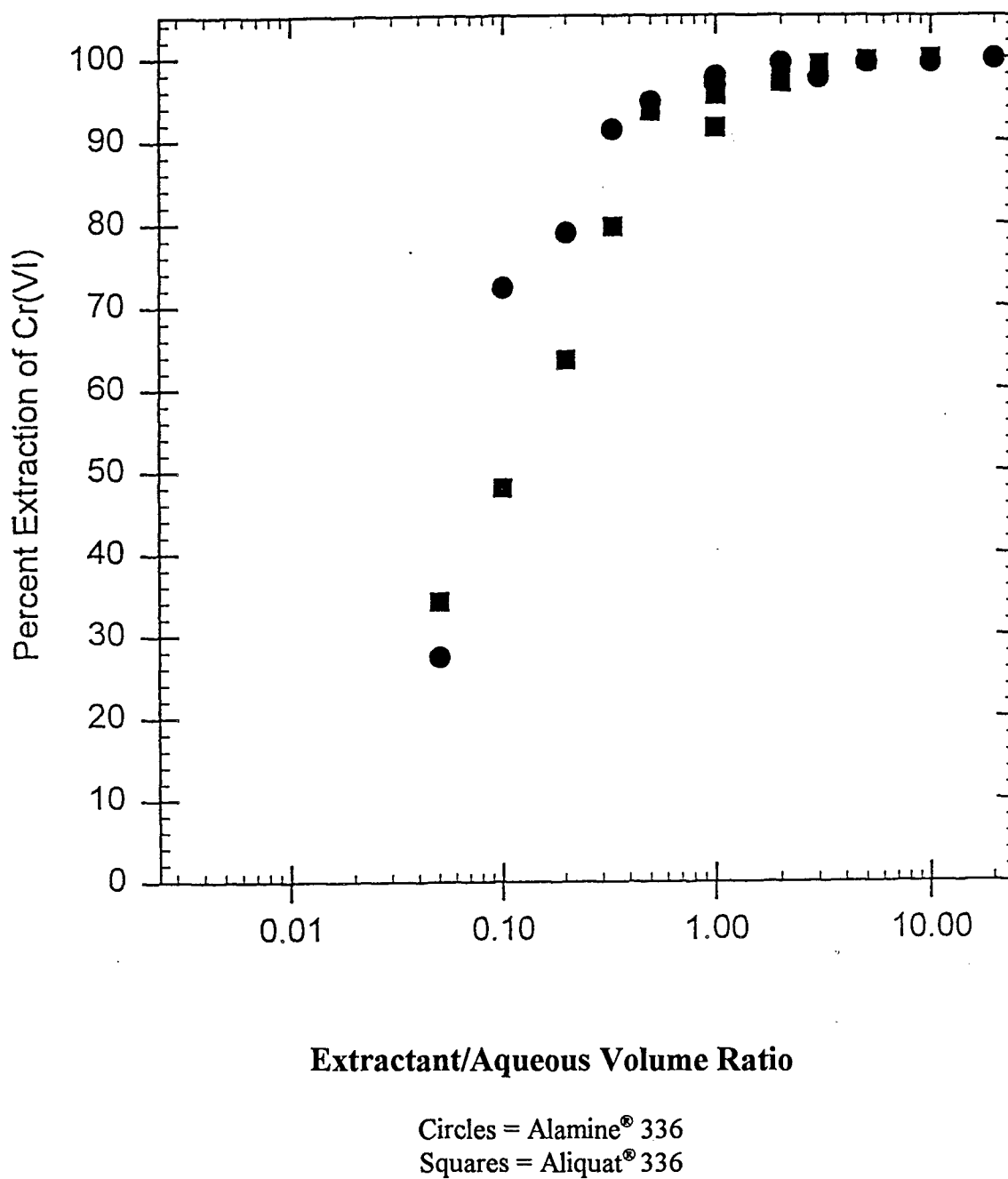


Figure 22. Hexavalent Chrome Removal from Synthetic Feed Water Using A-LIX.

**TABLE 38. MATRIX MATCHED HEXAVALENT CHROME
EXTRACTION RESULTS (47528-70, 74).**

Extrac tant ⁽⁴⁾	Feed Source	E/A	10 ppm Cr ^{VI} Spike?	[Cr] Feed ppb	[Cr] ⁽¹⁾ Raffinate ppb	pH ⁽²⁾ Raffinate	E Chrome Extracted (Cr) ^(3,5) %
Alamine [®] 336	Cr Sump	0.2	Yes	18,240	1130	2.54	93.8
	Cr Sump	2.0	Yes	18,240	1130	4.09	93.8
	Cr Sump	0.2	No	9,090	874	2.98	90.4
	Cr Sump	2.0	No	9,090	715	4.08	92.1
Aliquat [®] 336	Cr Sump	0.2	Yes	18,240	2130	7.42	88.3
	Cr Sump	2.0	Yes	18,240	928	9.02	94.9
	Cr Sump	0.2	No	9,090	784	8.47	91.4
	Cr Sump	2.0	No	9,090	208	7.30	97.7

- (1) Time for phase separation = 15-55 sec (one at 120 sec) with Aliquat® 336 slower than Alamine® 336 by 2 times.
- (2) pH (feed) = 8.27 for Cr Sump and 8.54 for equalization basin.
- (3) The raffinates had a light green tint, suggesting that some of the Cr is present as Cr^{III}.
- (4) The extractant composition in both cases was 20.0 percent amine, 5.00 percent Exxol® 10, and 75 percent aromatic 150.
- (5) Note: %E = 100 q/[q+(V_A/V_e)], where q = [Cr]_E/[Cr]_A, where [Cr]_E = ([Cr]_{feed} - [Cr]_{raffinate})(V_A/V_e).

However, the actual IWTP feed streams were found to have a pH of about 8.5 (Table 30). Since the Alodine baths are normally acidic, this high pH suggests that either >99.9 percent of the water in the stream represents tap water, or the Cr sump stream had been mixed with an alkaline stream, or some of both had occurred. At this higher pH, it was found that Alamine® 336 failed to provide good hexavalent chrome extraction, while the performance of Aliquat® 336 was little changed (Table 38). This is the expected impact of pH on these extractants (see introductory discussion). Therefore, if Alamine® 336 is to be used, then it should be applied to the stream while it is still acidic, or Aliquat® 336 should be used, or the stream should be made acidic.

The laboratory results were used to develop the design basis for a conceptual flow sheet (Figure 23) for an A-LIX process. The following design basis was selected.

(1) *Number of Stages.* The phase equilibrium data were used to prepare M-T plots (Figures 24 and 25). The M-T plots indicated that two extraction stages were needed for the Cr^{VI} extraction application.

(2) *Extractant Selection.* Alamine® 336 has the advantage of providing very high impurity concentration factors, but requires an acidic (~pH 2-5) Cr^{VI} feed solution and consumes acid and basic chemicals. Aliquat® 336 extracts Cr^{VI} over a broad pH range, but may not yield as much impurity concentration enhancement as does Alamine® 336. Therefore, either extractant could be used with these tradeoffs to consider.

(3) *Extractant Concentration.* Although 20 percent extractant level was used in the routine screening tests, the very low levels of Cr^{VI} present in the feed water should allow substantial reduction in the extractant concentration. Process optimization should test 1-5 percent concentrations, perhaps even lower for Alamine® 336.

(4) *Equipment Selection.* Liquid-liquid contactors come in a variety of types, for example, mixer-settlers, columns, centrifuges, mixer/oil skimmers, and constant, stirred-tank reactors (CSTRs). The specific contactor to recommend will depend on the specifics of the optimized process and so cannot be chosen here. The contactor is depicted in Figure 21 in general terms as a "mixer" and a "settler" each for extraction and stripping (extractant regeneration).

The economics of A-LIX relative to other options of Cr^{VI} removal are discussed at the end of Section VI.

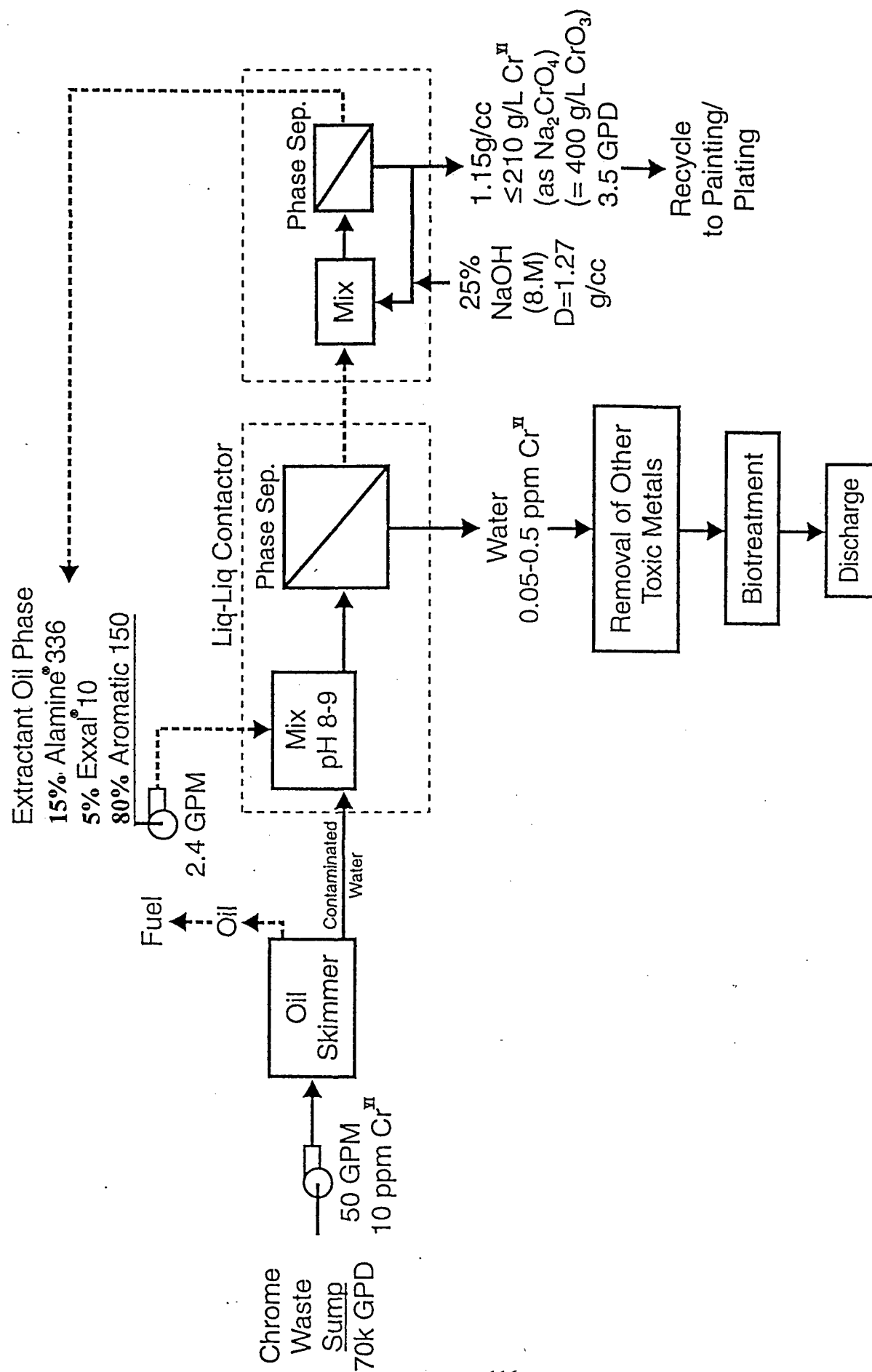


Figure 23. A-LIX Process Concept for Removal of Hexavalent Chrome from the IWTP Chrome Sump Aqueous Stream (Ref: OC-ALC IWTP).

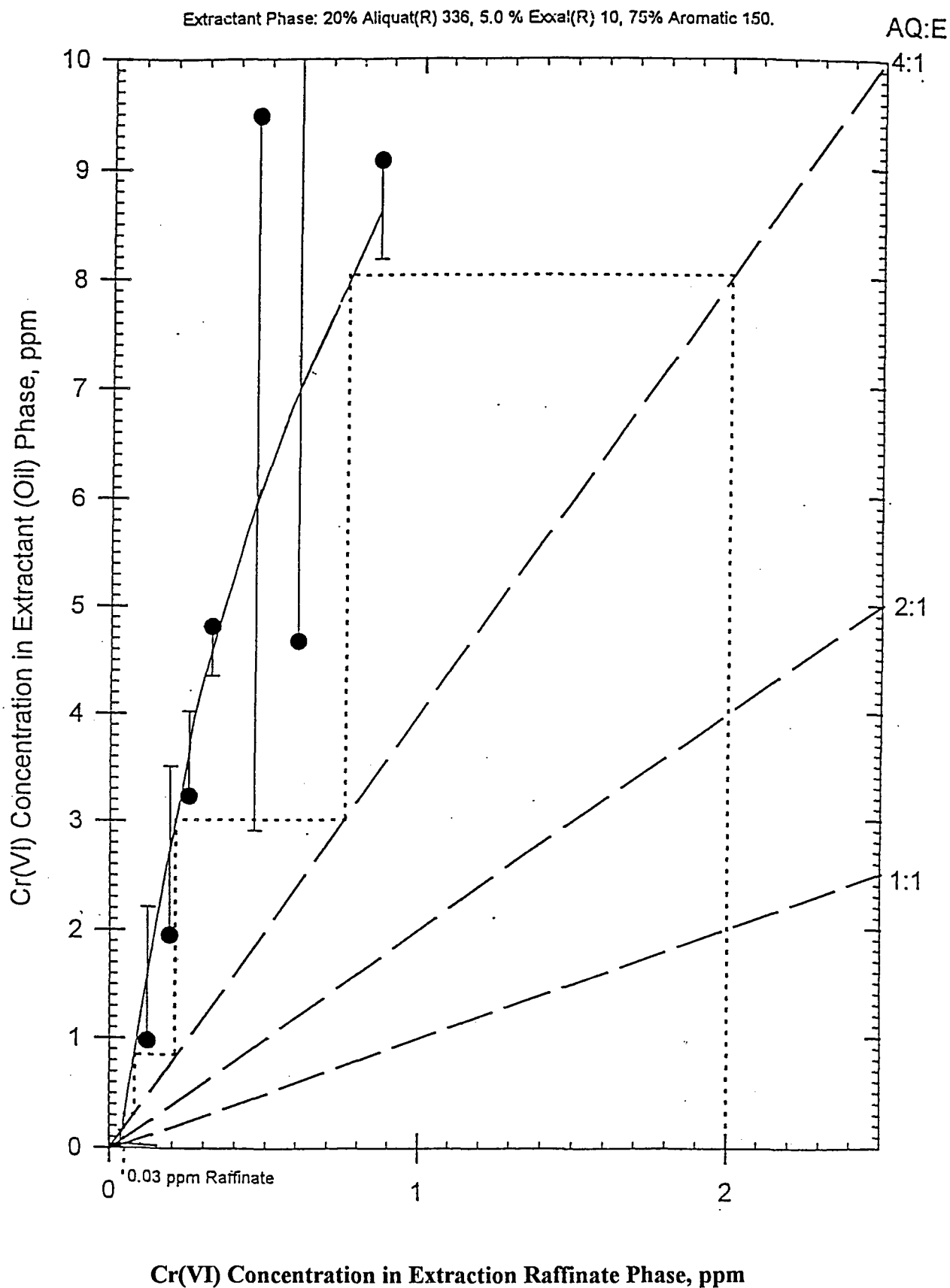


Figure 24. McCabe-Thiele Plot for Hexavalent Chrome Removal from Synthetic IWTP Feed Water Using Aliquat® 336 and A-LIX.

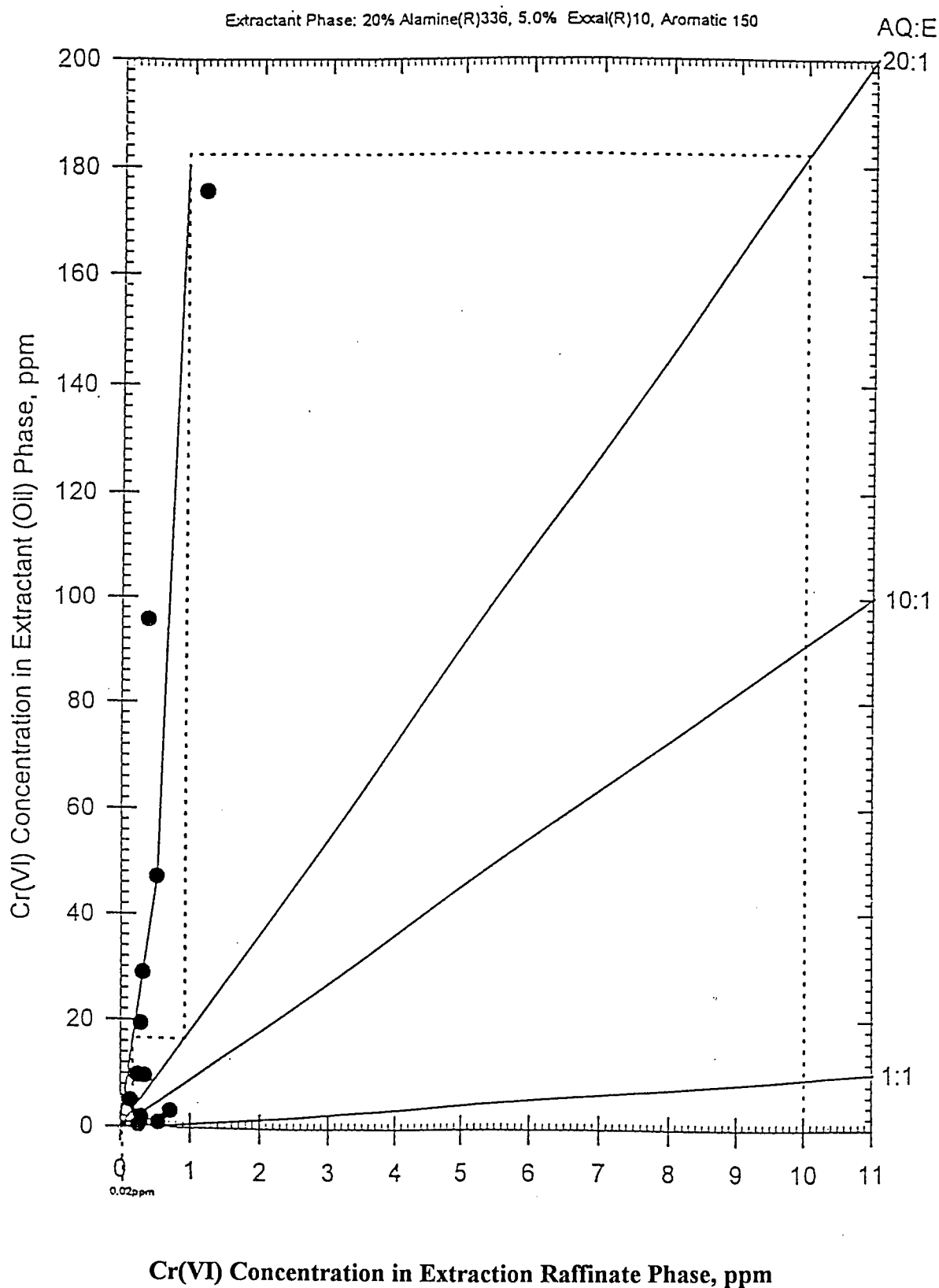


Figure 25. McCabe-Thiele Plot for Hexavalent Chrome Removal from Synthetic IWTP Feed Water Using Alamine® 336 and A-LIX.

**E. EVALUATION OF OPTIMIZED PRECIPITATION METHODS
WITH USE OF SOLIDS CONTACT CLARIFIER FOR TOXIC
METAL ION REMOVAL FROM IWTP PLANT INFLUENT**

**1. Technical Description of Improved
Metal Precipitation/Clarification**

a. Background

AF OC-ALC and WR-ALC IWTPs, the metal ions are removed by adjusting the waste water pH and then passing the stream through a solids contact clarifier (SCC). The SCC provides a blanket of active solids which provide absorption surface and particulate trapping mechanisms for the low level metal ion impurity ions and particles, respectively. Both hydroxide and sulfide type solids can be gathered in this manner. Traditionally the blanket consists of freshly precipitated (active) $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$. $\text{Fe}(\text{OH})_3$, used at the AF-ALC's, is especially effective as this blanket due to its broad pH stability ($\text{pH} \sim 3-12$), and because of its low solubility ($\sim 3 \times 10^{-8}$ M, 2 ppb). Critically, $\text{Fe}(\text{OH})_3$ also indiscriminately absorbs ions from solution thereby removing toxic metal ions such as Cr^{3+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , etc. Anions are also absorbed such as F^- and HPO_4^{2-} . However, with ferric and aluminum based coagulants, it is important that most (ca $\sim 50-90$ percent) of the solids be the coagulant and this adds substantially to the bulk of the waste. $\text{Al}(\text{OH})_3$ functions similarly to $\text{Fe}(\text{OH})_3$, but is effective over a narrower pH range (pH range $\sim 5-8$ with minimum solubility at $\sim 3 \times 10^{-7}$ M, 9 ppb). The aluminum floc is also colorless/white and so sometimes offers an appearance advantage. $\text{Fe}(\text{OH})_3$ self dewateres better than $\text{Al}(\text{OH})_3$ and so tends to have a higher bulk density than $\text{Al}(\text{OH})_3$, which is an economic advantage factor in dewatering operations downstream and/or in the volume of material sent to landfill.

b. Description of the Need

The need by the AF-ALC's is to reduce the weight of the sludge which emanates from the metal hydroxide precipitation process of the IWTP operation. Most (50-90 percent) of the dry weight of this sludge for the AF-ALC's (except Ogden) is the added $\text{Fe}(\text{OH})_3$.

Hence, there is a need to test the best impurity removal that can be accomplished by metal hydroxide precipitation without the use of large amounts of $\text{Fe}(\text{OH})_3$ coagulant/flocculant.

c. Description of the Technical Problem

Removing the $\text{Fe}(\text{OH})_3$ from the process to decrease sludge weight raises processing problems. The toxic metal ions of concern do not show the broad pH window of hydroxide precipitate formation or high insolubility as does $\text{Fe}(\text{OH})_3$ (Figure 26). What is more, these impurities arrive at the IWTP plant equalization tank very dilute (<10 ppm), and so the metal hydroxide flocs are slow to form and settle without the aid of the gathering properties of $\text{Fe}(\text{OH})_3$. The large volume of water sent to the IWTP daily (~ 1 million gpd) prohibits the use of ion exchange resin beds, normally the method of choice for such dilute streams, due to the cost of the large bed volumes that would be needed.

d. Approach

Solids Contact Clarifiers (SCCs) provide a mode of operation which overcomes the slow rate of hydroxide precipitation of dilute metal ions. This is accomplished by providing a blanket of freshly precipitated (active) metal hydroxide through which the pH adjusted metal impurities must pass. The blanket provides a highly porous, chemically similar adsorbent for these dilute metal hydroxides which promotes their ready absorption.

Although the metal contaminants do not show the broad pH operating window that $\text{Fe}(\text{OH})_3$ does, a number of them, especially $\text{Cu}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ (Table 39) form very insoluble hydroxides over a narrower pH window. These hydroxides would also tend to scavenge more soluble metal ion. However, currently there is not a control (buffer) for pH at this narrower pH window (8.8-9.2, Figure 26 and Table 39). Therefore, an introduction of a small amount of the appropriate buffer in addition to SCC operation may provide this pH control.

SCC chemistry using sludge blankets made without use of $\text{Fe}(\text{OH})_3$ can be simulated in the lab for batch screening studies by employing a stirred beaker with constant rpm mixer and a freshly prepared metal hydroxide blanket. The active metal precipitate blanket is formed when a solution containing metal contaminants is adjusted to the proper pH, then the

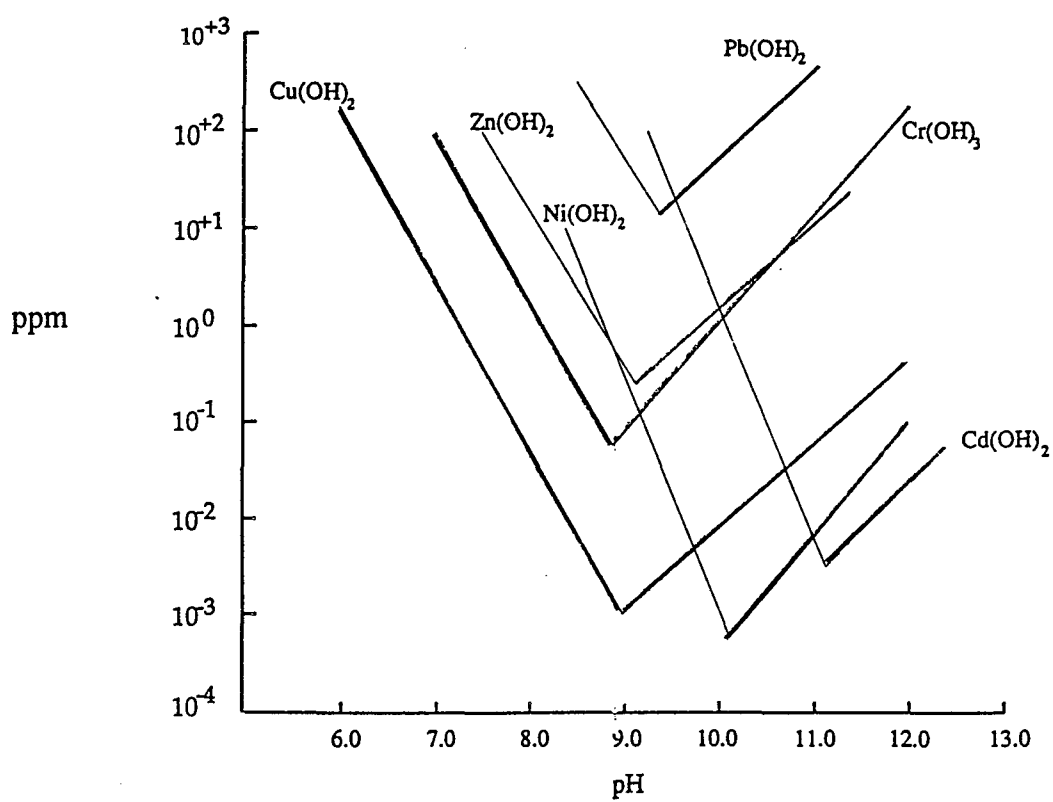


Figure 26. Solubility of Metals Ions in Water as a Function of pH (from Reference 1).

TABLE 39. THEORETICAL PRECIPITATION RESIDUALS, pH WINDOWS, AND OPTIMUM pH VALUES FOR IWTP METALS.

Minimum Concentration Possible (pH Range)		Toxic Metal Ion Contaminant	Inlet Concentration (ppm)	Target Max Outlet Concentration (ppm)	Precipitation		
					Range		Concentration M, ppm
					pH		
					Ref: J. Kragten (Cushnie)		
M	ppm/ppb						
< 10 ⁻⁸ (8.8 - 10.7)	0.64 ppb	Cu ^{II}	2	0.05	7.5 - 12.1 (9.20)	10 ^{-6.1} , 0.1 ppm (10 ppm)	
10 ^{-5.8}	82 ppb	Cr ^{III}	5	0.10	8.6 (8.0 - 9.5) (8.9)	10 ^{-5.7} , 0.1 ppm (.07 ppm)	
1.0 x 10 ⁻⁷ (11 - 12.5)	11.2 ppb	Cd ^{II}	2	0.02	10.7 - 12.6 (11.2)	10 ^{-6.7} , .02 ppm (.005 ppm)	
10 ⁻⁴	21 ppm	Pb ^{II}	2	0.10	10.1 - 10.7 (9.3)	4.8 x 10 ⁻⁷ , 0.1 (20 ppm)	
10 ⁻⁵	0.65	Zn ^{II}	2	NA	8.5 - 10.5 (9.1)	10 ^{-4.9} , 0.65 (0.3)	
10 ^{-5.8}	93 ppb	Ni ^{II}	2	0.5	9.3 - 11.5 (10.1)	10 ^{-5.1} , 0.5 (0.8)	
10 ⁻⁷	5.6 ppb	Fe ^{II}	0	NA	10.6 (9.7 - 12) (NA)	10 ⁻⁶ , 0.056 (NA)	

NA: Not applicable.

contents are allowed to settle, and the supernatant discarded. The contaminated water is then added to this freshly formed, slowly stirring blanket with concomitant pH adjustment.

Important parameters which affect the performance of metal precipitation are composition of the blanket, time, temperature, pH, precipitation chemistry, mixing intensity and the number of contacts/blanket depth. Of these factors, only temperature and blanket composition are not adjustable in the commercial operation. (Composition is adjustable when ferric salts are added to prepare the blanket.)

The batch mode of testing used in these lab screening test provided the best metal removal that a particular SCC system and use conditions could achieve. Depending on design and operation conditions, a continuous flow through system could be as good or worse due to short circuiting, insufficient residence time, fluctuations in pH, insufficient or over mixing, etc.

2. Test Facilities and Procedures for Improved Sludge Blanket

a. Apparatus

The apparatus shown in Figure 27 was used for batch testing of added iron free SCC and precipitation chemistries. All components contacting the test solution were cleaned with warm MICRO[®] cleaning bath and thoroughly rinsed with DI water before each experiment.

b. Chemicals

The toxic metal ion impurities of concern for this work are listed in Table 38 along with the inlet concentration, outlet concentration target, and pH for maximum precipitation of the metal hydroxide. The initial conditions for each SCC simulation test was to add 10.00 ml of a 100X concentrated IWTP inlet solution to 990.0 ml of water and adjust the pH to form the slurry/(SCC blanket) as described below.

c. Experimental Procedures

An active metal hydroxide absorbent was prepared to simulate the SCC blanket. A synthetic influent was prepared (see Table 40) and added to the SCC suspension in accordance with the detailed procedures provided in Appendix C. The suspended solids were

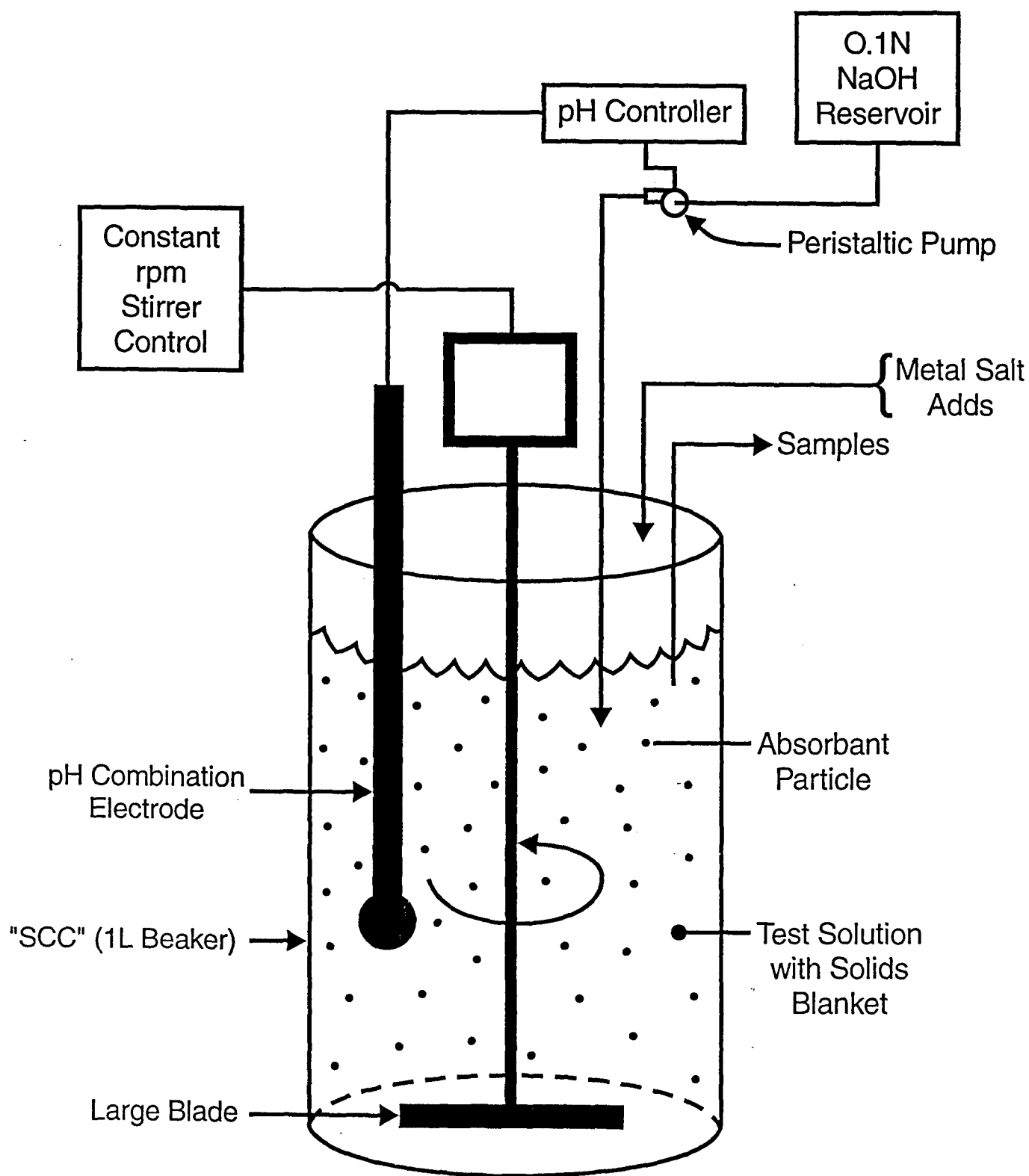


Figure 27. Laboratory Apparatus Used for Metal Contaminate Removal from Water by Precipitation.

allowed to settle and a sample of the supernatant was analyzed for metals. The Test Results are presented in Table 41.

3. Test Results for Improved Metal Precipitation/Clarification

Table 41 summarizes the impurity removal screening test results for the case where solids contact clarifier conditions employing a blanket prepared from impurities only are used to remove metal ion impurities rather than a blanket prepared from iron salts. Table 42, provides, in addition to SCC results, the precipitation results where a SCC blanket was not specifically used but the products were centrifuged for 10 min then passed through a 0.02 μm filter to simulate the ultimate effect of an SCC. Table 42 includes the results for pH adjustment only (metal hydroxide precipitation), phosphate precipitation (to target Cr^{III} removal), thio-based precipitation (to target Cu, Cd, and Pb removal), as well as blank and reference information. Table 43 provides the data which separate the pH and thio effects. TMT was used for these tests as it is stable over the pH range needed to differentiate metal hydroxide precipitation from metal-thiol precipitation.

Table 44 represents test data for metal hydroxide precipitation using spiked actual IWTP feed. This table also contains data on ICP repeatability using DI water and on filtered vs. Unfiltered feed solutions.

4. Technical Evaluation of Improved Metal Precipitation/Clarification

a. Hydroxide Precipitation

Hydroxide precipitation was found (Table 41) to be very effective at precipitating toxic metals in batch operations with the synthetic IWTP feed provided the pH was adjusted to $\text{pH } 8.9 \pm 0.1$ and chelating agents were absent. The pH range may be expected to be only slightly larger than this after optimization. As expected, the completeness of precipitation is the same whether an SCC blanket is present or not. However, the processing time and control constraints at the IWTP would favor the use of an SCC.

**TABLE 40. MATERIALS AND AMOUNTS USED FOR PREPARATION
OF SYNTHETIC IWTP INLET FEED.**

Metal	Metal Salt	Purity	Formula Wt.	mg/L Salt Needed for 200 ppm Metal Ion (500 ppm for Cr)	Supplier
Cu ²⁺	CuSO ₄ •5H ₂ O	98+%	249.60	786 mg	Aldrich
Cr ³⁺	KCr(SO ₄) ₂ •12 H ₂ O	98+%	499.40	4802 mg	Aldrich
Cd ²⁺	CdSO ₄	99%	208.46	372 mg	Aldrich
Pb ²⁺	Pb(OAc) ₂ •3H ₂ O	99+%	379.33	366 mg	Aldrich
			TOTAL:	6326	

**TABLE 41. PRECIPITATION OF METAL ION IMPURITIES AT pH 8.9±0.1
USING SOLIDS CONTACT CLARIFIER. (47528-26)**

Sample # 47528- 26-X	Reaction Time with SCC Blanket (min.)	Metal Ion				Fraction Metal Removed %			
		Concentrations (ppb)							
		Cd	Cr ^{III}	Cu	Pb	Cd	Cr ^{III}	Cu	Pb ^(a)
1	Filtered Feed	1670	4490	1810	1710	--	--	--	--
2	0	11	< 9	18	<15	99.3	99.8	99.0	> 99.1
3	5	22	< 9	15	<15	98.7	99.8	99.2	> 99.1
4	20	15	15	19	23	99.1	99.7	99.0	98.7
5	40	24	17	24	50	98.6	99.6	98.7	97.1
6	80	17	13	24	44	99.0	99.7	98.7	97.4
7	171	17	18	29	57	99.0	99.6	98.4	96.7
NPDES Lmit	--	20	100	50	100	-	-	-	-

(a) Includes Pb precipitated as PbSO₄.

TABLE 42. METAL IMPURITY PRECIPITATION TEST RESULTS^(a).

Test #	Additive	pH	Metal Concentrations (ppb)				
			Cd	Cr	Cu	Pb	
Feed	Feed	-1	2-3	1640	4220	1670	1580
		-2		2040	4500	2130	2100
		-3		1680	4360	1690	1500
	Hydroxide (5-165 min)	8.9	<5	<12	22	<6	
	Insoluble starch xanthate ^(b) (5-10 min) (80-160 min)	8.9	<5	16	34	<6	
			<5	<12	42	<6	
	HPO ₄ ⁼ (5 min)	8.9	30	173	12	8	
	HPO ₄ ⁼ (160 min)		25	73	<11	13	
	NALMET® 8702 (Soluble poly thiocarbamate) ^(b) (5-10 min) (160 min)	8.9	<1	150	13	<1	
			2	24	27	<1	
	SCC (5-10 min) (40-160 min)	8.9	19	7	17	12	
			19	15	26	50	
	Blank (Water)	7	<5	<12	<4	<6	
	Detection Limit	-1	-	1	6	2	1
		-2	-	5	12	4	6
	Filter Test (of 10X diluted feed) - unfiltered - filtered	3	169	459	190	154	
		3	167	451	191	149	
NPDES	Target	-	20	100	50	100	

^(a) Conditions: pH 8.9, one contact, 5-160 min mix time (six samples). Samples centrifuged and 0.2 µ filtered. Exactly 6.00 ml sample acidified with 1.000 ml 6.0 N HNO₃. Error ~ ± 5 ppb. Synthetic feed.

^(b) Note that poly thio precipitants are added at 3-40 times impurity weight.

**TABLE 43. pH DEPENDENCE OF TOXIC METAL ION REMOVAL
BY PRECIPITATION USING A LOW-pH STABLE
THIOL AGENT, TMT.**

Sample No.	Metal Ion Concentration (ppb)								pH
N.B # 4752 845-	Cd		Cr		Cu		Pb		
	5 min	60 min	5 min	60 min	5 min	60 min	5 min	60 min	
1, 2	1220	1070	4270	4400	30	47	14	6.5	4.96
3, 4	26	12	1500	667	41	48	<2.7	<2.7	6.95
5, 6	<9	<9	247	149	41	46	<2.7	4.1	8.94
Feed	1640		4220		1670		1580		3
D.L.	9	9	6	6	24	24	2.7	2.7	-

**TABLE 44. METAL HYDROXIDE PRECIPITATION TEST RESULTS
USING ACTUAL IWTP FEED (SPIKED) AND PRECISE pH
CONTROL (47528-63, 66).**

IWTP Stream	Sample I. D.	pH	Metal Concentrations (ppb)			
			Cd	Cr	Cu	Pb
Cr Sump (D3)	Unspiked Feed (not centrifuged)		<7	5380	<20	<7
	Unspiked Feed (centrifuged/ filtered)		<7	5190	26	<7
	Feed (spiked)		1650	13,700	1840	1590
	5 min at pH 8.9	8.82	157	5220	182	145
	15 min at pH 8.9	8.93	91	4730	67	54
	25 min at pH 8.9	8.99	81	4850	91	47
	45 min at pH 8.9	9.01	78	4990	90	63
	85 min at pH 8.9	9.04	79	4860	96	62
	180 min at pH 8.9	9.07	85	4960	95	69
Equali- zation Basin	Feed		<7	19	<20	<7
	Feed (centrifuged/ filtered)		<7	32	<20	<7
	Feed (spiked)		1690	4980	1920	1590
	5 min at pH 8.9	8.99	30	13	24	19
	10	9.00	30	20	22	19
	20	9.00	29	33	<20	20
	40	9.04	32	13	31	22
	85	9.10	35	27	30	24
	170	9.11	34	<11	31	24
DI Water			<7	<11	<20	<7
			<7	<11	<20	<7

Tests using actual IWTP feed (Table 44) illustrate that metal hydroxide precipitation also works for the actual plant stream matrices with two important differences. First, as expected, chrome sump stream clearly contained about 5,000 ppb of Cr^{VI} which does not precipitate as it does not form a neutral metal hydroxide. Prior reduction to Cr^{III} (current practice) but only using a stoichiometric amount of ferrous salt, or A-LIX removal of Cr^{VI} , would be needed prior to metal hydroxide precipitation. Second, the residual metal contaminant levels for the chrome sump (D3) IWTP sample is a little higher than what was found for the synthetic stream. The D3 stream is known to contain low levels of phenols. It is well known that phenol complexes metal ions at pH 9, and therefore could be causing this observed residual metal concentration. Although this stream could be treated using a thio polymer precipitant in a post hydroxide precipitation polishing step, it is unlikely that this would be needed upstream of the primary precipitation treatment of the equalization tank overflow.

On the other hand, the behavior of the equalization tank stream closely mirrored that obtained for the synthetic IWTP streams (compare Tables 41 and 42 with 44).

b. pH Control in Metal Hydroxide Precipitation

A critical process control issue was found in that normal waste waters are not buffered at the $\text{pH } 9.0 \pm 0.2$ region making it difficult to control the pH at this set point. Therefore, the process will tend to undershoot/overshoot the pH which leads to toxic metal resolubilization/incomplete precipitation, especially visible at the low ppm compliance range.

Options for alkaline side buffers are phosphate, carbonate, phenol, alkyl amines, ammonia, and borate. Only the latter two are effective at $\text{pH } 9.0 \pm 0.5$. Ammonia has a severe odor problem and it may complex (redissolve) metals. This leaves borate as the recommended buffer to use. Borax (sodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$) is a common source for borate based cleaners, etc. which may be reasonable to use from an environmental and biotreatment plant tolerance stand point. However, exact site compliance issues would need to be checked before any borate additions are considered. About a 4.0 ppm feed rate or 290 lb of borax (33 lb B) per day is estimated to be a reasonable starting point for evaluating the benefits of buffer control of pH adjustment (0.00032 lb borax/gallon water treated,

or 9 g borax per 625 gallons of water treated). The alkalinity value of borax will offset a small portion of the cost of the caustic used for pH adjustment. The actual buffer system which would control the pH at 9.0 ± 0.1 is boric acid/borate ($\text{B(OH)}_3/\text{B(OH)}_4^-$). The major value of using a buffer is in achieving compliance residual metal levels with less caustic/acid consumption and the labor savings associated with dealing with difficult pH control.

c. Coagulation and Flocculation in Metal Hydroxide Precipitation

We examined both unaided precipitation of impurities and the use of a solids contact clarifier "blanket" of metal hydroxide solids produced fresh from a 100X concentrate of the same 4 metal (Cu, Cd, Pb, Cr) synthetic IWTP feed solution used for Sections VI.C and VI.D. The results of both tests were equivalent (Tables 41 and 42) in achieving dischargeable levels of residual impurities. This surprising result strongly suggests that metals other than iron can facilitate (via coagulation and flocculation mechanisms) the removal of more soluble contaminant ions provided the pH is controlled well. From the solubility vs. pH curves (Figure 25), we conclude that the more insoluble metal hydroxides (Cu(OH)_2 and Ni(OH)_2) could be used to facilitate the removal of the more soluble metal hydroxides (e.g., Pb(OH)_2 , Cr(OH)_3).

d. Metal Contaminant Precipitation using Thio-Polymers

The test results in Table 42 confirm that metal ion impurities are effectively removed when polymeric thiols are added to the contaminated water at pH 9. However, these commercially available precipitants, based on xanthates and thiocarbamates, are unstable at pH values less than about 8. Therefore, it was not clear from these tests whether the metals were being removed by the thiol, by hydroxide ion precipitation, or by a combination of the two.

This pH effect issue was resolved by testing an acid compatible thio precipitant, TMT (2,4,6-tri-mercapto-s-triazine, Degussa, Inc.). Three pH values were tested, 5, 7, and 9 (Table 43) to cover the range from stable solutions of the metal ions (pH 5) to where the ions are effectively precipitated as the hydroxides (pH 9). The metal removal results are also given in Table 43. These results indicate that there is essentially no pH dependence for the removal of Cu and Pb by the thiol precipitant. The pH 5 data indicate that these two metal ions

are clearly removed as the thiol compound since their hydroxide precipitates do not form until above this pH.

Cadmium removal in the presence of TMT displays a strong pH effect. Very little Cd precipitates at pH 5, but it is removed to below discharge limits by pH 7. This pH is far below that possible for cadmium hydroxide precipitation (~pH 10), and so must be attributed to thiol induced precipitation.

Chromium on the other hand shows no enhanced removal by the thio precipitant and instead displays a precipitation pattern expected for chromium(III) hydroxide. This effect is well understood and is due to the very slow (about a week) ligand exchange rate of the Cr(III) ion at ambient temperature and mild pH. Hence, the thiol cannot quickly bond to the Cr(III) to facilitate its removal. All thiols are known to display this behavior. Heating and/or long (days) reaction times would be needed to obtain Cr^{3+} removal by thiol precipitation.

It is concluded that thio-based precipitants have a marked effect on broadening the pH window for removal of many metal ions, for example, Cu, Pb, and Cd. However, pH adjustment will still be required to remove certain metal ions, especially Cr^{III} , and to enhance the removal of others, e.g., Cd. Therefore, since thiols add significant weight to the sludges they produce (due to the higher atomic mass of S relative to O), since hydroxide precipitation is also still required, and since these polymers are costly, we confirm that the role of these reagents should be kept as a polishing agent and not as a primary metal precipitant.

e. Cr^{3+} Precipitation as the Phosphate, $\text{Cr}^{\text{III}}\text{PO}_4$

Chromium(III) ion, Cr^{3+} , is very effectively removed by the current ferric hydroxide coagulation/flocculation process. However, chromium hydroxide has significant solubility (Figure 26). Therefore, care is needed that Cr^{3+} is efficiently precipitated if ferric salt addition is stopped. At times, there may be insufficient Cu^{2+} and/or Ni^{2+} impurities to scavenge the Cr^{3+} in the low Fe blanket. CrPO_4 is very insoluble and the tests (Table 42) show that CrPO_4 precipitation removal may be sufficiently effective for the removal of Cr^{3+} contamination but also that slower precipitating colloids may form. The key will be to determine the minimum phosphate concentration (to avoid anionic colloids) needed to reduce Cr^{3+} to acceptable levels in the

residence time of the process (mixing station plus solids contact clarifier). Excess phosphate would be beneficial to the biotreatment operation. For 10 ppm of Cr^{3+} , 18 ppm of PO_4^{3-} would be removed with it. Any additional phosphate may speed the rate of Cr^{3+} removal, but would not report to the metal hydroxide sludge as CrPO_4 . Note that other insoluble phosphates may also form, for example, those of aluminum, silver, calcium, cadmium, cobalt(II), copper, iron(III), nickel, lead(II), and zinc. The phosphate solids may behave better than the hydroxides in terms of lower water retention. Since Cr is the major toxic metal ion from the chrome sump, these other phosphates are expected to be minor. Alternatively, phosphate could be added as a part of a polishing post treatment, for example with polymeric thiol precipitants, without concern for interference. Suggested forms for the phosphate are as phosphate based fertilizer (ammonium or potassium based, but not calcium-based as in bone meal), TSP (trisodium phosphate), phosphoric acid, etc.

f. Proposed Flow Scheme for Metal Contaminant Removal by Precipitation

Figure 28 represents the proposed process flow scheme for impurity removal by precipitation. Most if not all of the hardware is already in place at OC-ALC and WR-ALC IWTPs, the two large users of ferrous sulfate for metal reduction. The proposed process change is one of optimization and enhanced control while at the same time removing the need to use large quantities of iron salts and associated neutralization base (caustic or lime).

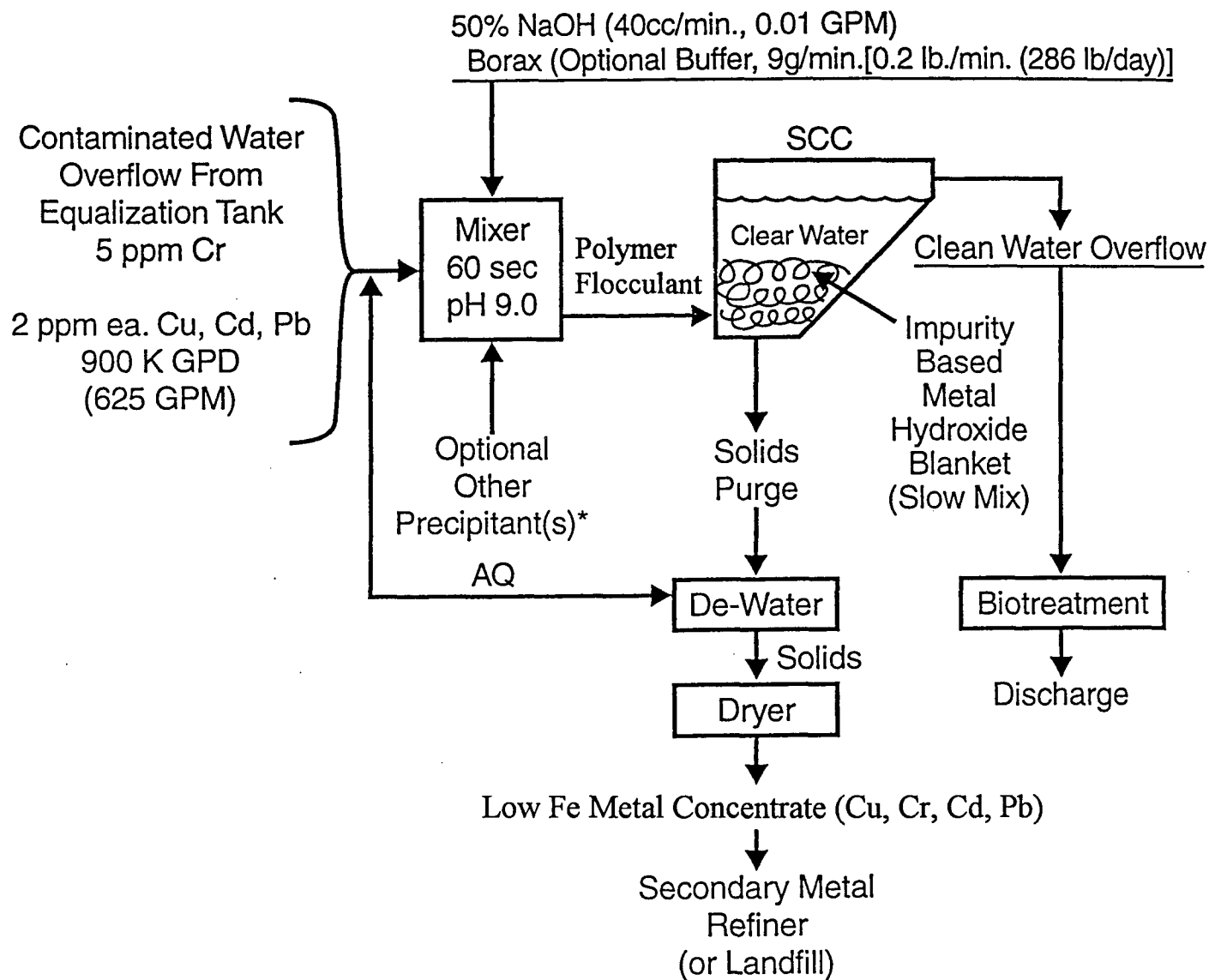
The feed to the process is the equalization basin overflow (OC-ALC example) previously treated with a stoichiometric amount of ferrous sulfate (or acidic sulfite) to convert the Cr^{VI} content into Cr^{III} . (Alternatively, A-LIX can be employed to remove Cr^{VI} .) No additional iron salts are recommended for coagulation and flocculation. Instead, the SCC blanket is prepared from the impurities in the stream. This blanket could be prepared by slowly flowing the feed water through the SCC, or better still, initially charging in ferric sulfate to create a "starter" blanket. It is critical that the SCC blanket purge slurry rate be cut back substantially (~50 - 90 percent) to avoid removing too much of the blanket from the SCC. This cut in purge rate reflects the lower sludge production rate of the proposed process.

pH control is difficult in the current process. This is largely compensated for by the use of a large volume of ferric salts and base which can absorb metals over a broad pH range. In the proposed process only the base needed for impurity precipitation is used. However, the pH control will be similar as before. Therefore, we suggest the addition of borax at the rate of about 0.2 lb/min (4 ppm) into the feed solution upstream of pH adjustment. The alkalinity of borax will reduce the caustic consumption accordingly and the resultant boric acid/borate buffer will enable good pH control at $\text{pH } 8.9 \pm 0.2$. Higher borax concentrations will increase pH control still further but with additional raw material cost. A critical aspect of the process is that the more soluble metal hydroxides, for example Cd and Pb, are rendered insoluble by virtue of their being absorbed into the more insoluble metal hydroxides, for example those of Cu^{II} and Cr^{III} . The screening tests followed the precipitation/dissolution rate for up to 160 min. Precipitation was complete in 5-10 min. However, precipitation was slower, especially for Cr^{III} , when certain additives (e.g., orthophosphate or Nalmet® 8702) were introduced. The vendor recommends that if this metal precipitant is used, that it be added after pH adjustment with a 20-30 min residence time before the stream enters the SCC.

F. REDUCED FERROUS SULFATE USAGE WITH OXIDIZABLE ORGANIC

This was the last one of the four metal reduction concepts tested (see Table 28). The objective was to reduce ferrous sulfate addition to approximately one-third of the stoichiometric amount, and add instead an equivalent amount of methanol, an oxidizable organic which reacts with the Cr^{V} and Cr^{IV} intermediates involved in Cr^{VI} reduction. The concept was experimentally evaluated in the experiment described below.

A 9.94 ppm sample of Cr^{VI} solution was made in 1220 ppm in methanol and then treated with one-third the stoichiometric amount of ferrous sulfate [based on conversion of Cr^{VI} to Cr^{III} and Fe^{II} to Fe^{III}]. The test solution was sampled after each portion of Fe^{II} was added at pH 4.5. Each sample was then pH-adjusted to 8.9 and centrifuged to remove any Cr^{III} as $\text{Cr}(\text{OH})_3(\text{s})$. The 0.2 μ filtered samples were analyzed for Cr. For reference, an excess ($\text{Fe}/\text{Cr} > 3$) of ferrous sulfate was added to the product solution and sampled similarly. The results indicated that the



- *Effective Metal Precipitants:
- Nalmet[®] 8702 (Soluble Carbamate)
 - Insoluble Starch Xanthate
 - Phosphate Salt
 - TMT (2,4,6- Trimercapto-s-Triazine)

Figure 28. Broad Spectrum Metal Ion Removal Using Solids Contact Clarifier (SCC) Blanket Produced From Impurities with Buffering (Ref: OC-ALC IWTP).

methanol did not participate in the reduction of Cr^{VI} to Cr^{III} , and that the added Fe^{II} reacted 100 percent with the Cr^{VI} in a reaction stoichiometry of 3:1, i.e., exactly one-third of the Cr^{VI} was reduced to Cr^{III} .

While the above concept was unsuccessful, it was clearly demonstrated that only a stoichiometric amount of ferrous sulfate was needed to reduce Cr^{VI} to Cr^{III} . Therefore, the excess ferrous sulfate (i.e., Fe/Cr atomic ratio of 25 to 40) used at OC-ALC and WR-ALC must be associated with broad-spectrum metals (Cr^{III} , Cd, Ni, Pb, and Zn) removal rather than with Cr^{VI} reduction.

G. COMPARATIVE ECONOMIC ANALYSIS OF METAL REDUCTION OPTIONS

1. Process Options

The metal reduction needs of the AF-ALC IWTPs reduce to two cases: Cr^{VI} removal and broad spectrum toxic, metal ions (Cr^{III} , Cd, Pb, Cu, Zn) removal. The screening tests conducted during Phase I of this project suggest the following combinations of process to address both cases:

- (1) Use of a theoretical amount of ferrous sulfate to reduce Cr^{VI} to Cr^{III} followed by one of two process options to remove toxic metal ions:
 - (1A) Use of a more effective sludge blanket, i.e., one made primarily from impurity ions than from added ferrous sulfate, or
 - (1B) Use of MOS-LLX
- (2) Use of A-LIX to remove Cr^{VI} followed by one of two process options to remove toxic metal ions:
 - (2A) Use of existing SCC operation
 - (2B) Use of a more effective sludge blanket, or
 - (2C) Use of MOS-LLX

Note that in Step 1B, there are more metal cations to remove than in Step 2C, since A-LIX does not just convert Cr^{VI} to Cr^{III} but totally removes it.

2. Relative Impact on Sludge Quantity Reduction

The proposed process options contribute to an increase in capital outlay and equipment operating costs. These operating costs must be more than offset by the reduction in sludge disposal costs due to implementation of proposed process options. These sludge disposal cost savings can be estimated for OC-ALC and WR-ALC IWTPs using the data in Table 45. These data were used for economic analysis of various options.

As suggested by the data in Table 45, the maximum impact of implementing A-LIX for Cr^{VI} removal (i.e., Option 2A) is for IWTP Plant #2 at WR-ALC. The MOS-LLX (Option 1B) is equally impactful on Stream D3 at OC-ALC or IWTP Plant #2 influent at WP-ALC. These technologies can also be applied to Stream Lift #2 at OC-ALC and IWTP Plant #1 at WR-ALC, but these streams are 3 to 10 times larger, making the equipment cost, which is proportional to stream flow rate, much higher.

The implementation of improved sludge blanket concept does not require any capital outlay for metal reduction, so it is worth considering for all the IWTP streams both at OC-ALC and WR-ALC.

3. Capital Cost Estimation

The only capital cost for Option 1A (improved sludge blanket) is due to addition of a chemicals addition system. The purchased equipment cost (PEC) was estimated first, using information given in Section V.B.9. The fixed capital investment (FCI) was based on application of factors to PEC as discussed in Section V.B.9 as well^(25,26).

The A-LIX and MOS-LLX, involve similar mixer-settler equipment. The only difference between the two processes is that the extractants and extractant regenerants (stripping solutions) are different. These plants were costed on the basis of data from Bureau of Mines using the following formulae⁽²⁹⁾:

**TABLE 45. ESTIMATED CONTRIBUTORS OF VARIOUS WASTE WATER STREAMS
AND ASSOCIATED CONTAMINANTS TO SLUDGE GENERATION**

	OC-ALC IWTP		WR-ALC IWTP	
	Stream D3 (Painting/Depainting)	Stream Lift #2	Plating Shop (IWTP Plant #2)	Balance of IWTP (IWTP Plant #1)
Waste water flow rate, gpd	75,000	750,000	80,000	200,000
Amount of wet sludge ^(a) corresponding to RCRA metals, tons/yr				
-- Contribution due to Cr ^{VI} , tons/year	73	31	276	2
-- Contribution due to Cr ^{III} , tons/year	62	35	75	103
-- Contribution due to Rest of RCRA metals, tons/year	83	75	34	59
TOTAL	<u>218</u>	<u>141</u>	<u>385</u>	<u>164</u>
Maximum possible savings, \$/yr	78,622	50,586	169,464	72,164

^(a) Wet sludge solids content: 10% for OC-ALC and 31% for WR-ALC.

$$\text{PEC} + \text{Installation} + \text{Instrumentation} + \text{Piping} + \text{Electrical} = \quad (12)$$

$$\$382,979 (X)^{0.955} 0.249 (N)^{0.668} (\text{Inflation Factor})$$

where, X = flow rate to extractor, L/min

N = number of stages (2 in our case)

Inflation factor = 1043/804, using Marshal and Swift Index to 1st Qtr, 1996.

The FCI, which includes engineering and contingency was then calculated as follows:

$$\text{FCI} = (\text{PEC} + \text{Installation} + \text{Piping} + \text{Electrical}) (1.3) \quad (13)$$

The use of Equation (13) makes the cost factors for A-LIX and MOS-LLX comparable to factors used for estimating cost for other technologies (e.g., flocculation and drying).

To illustrate the equipment changes necessary to implement the proposed metal reduction technologies, the application of Option 1B, i.e., use of a theoretical amount of ferrous sulfate to reduce Cr^{VI} to Cr^{III} followed by MOS-LLX, as applied to IWTP Plant #2 at WR-ALC, can be considered. Figure 29 shows the IWTP subsystems impacted if Option 1B is implemented. The only ferrous sulfate needed is the theoretical amount needed to reduce Cr^{VI} to Cr^{III} . The changes in Section 2B of the IWTP are shown in Figure 30. Note that the use of a polymer to eliminate the use of lime for dewatering of the sludge will further reduce the disposal cost, but is shown as an optional step in Figure 29. A MOS-LLX system was sized at 282 L/min using the following basis:

- Operation is 24 hours/day, 7 days/week, 48 weeks/year
- 25 percent extra capacity to allow for surges in the flow rate

Using Equations 12 and 13, the FCI for Option 2A was estimated at \$84,000.

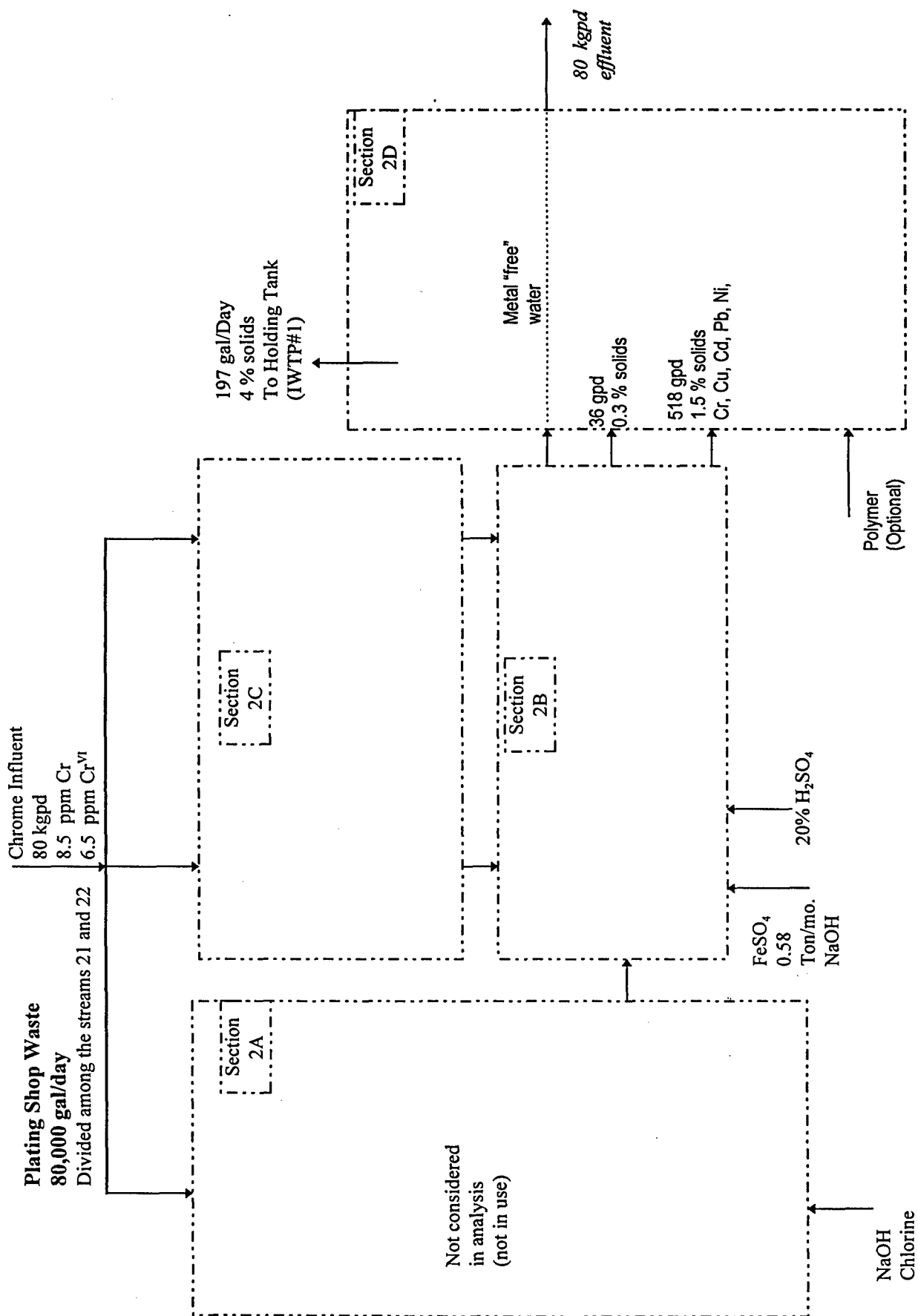


Figure 29. Plant Changes for Application of MOS-LLX at IWTP Plant #2 at WR-ALC.

4. Operating Costs and Payback Periods

a. Option 1B for WR-ALC IWTP Plant #2

Continuing with Option 1B, the operating costs for MOS-LLX were estimated using Bureau of Mines data as follows:

$$\begin{aligned}\text{Labor Cost} &= 0.142 (X)^{0.899} \\ \text{Supply Cost} &= 0.277 (X)^{0.988} 0.758 (N)^{0.133}\end{aligned}$$

These operating costs are included in Table 46. The total yearly operating costs are \$22,188 which are offset by savings of \$162,677 in sludge disposal costs. This leads to a payback period of 0.6 years.

b. Option 1A for OC-ALC

The economic analysis for Option 1A for OC-ALC is summarized in Table 47. The fixed capital cost for this case is small as only a process control system for addition of chemicals is needed. The plant changes for this option are shown in Figure 31.

c. Summary of Selected Options

Based on the use of A-LIX, MOS-LLX, and improved sludge blanket concepts, a number of combinations can be conceived based on which part of an IWTP an individual concept (e.g., A-LIX) is applied to. Several of these options with net cost savings for WR-ALC and OC-ALC are summarized in Table 48. Clearly, if the option 1A employing a more effective sludge blanket can be shown to work, it is the most economical one. If, however, this concept is not practical, then A-LIX and MOS-LLX should be considered. The most economical use of A-LIX is for WR-ALC IWTP Plant #2 (plating shop effluent) because of the large fraction of Cr^{VI} in it. And MOS-LLX is economical for OC-ALC Stream D3 (painting and depainting effluent) because of a relatively large portion of Cr^{III} and other RCRA metals. Clearly, A-LIX and MOS-LLX can be combined, preferably at the point where concentrations of impurities are the highest.

The preferred metal reduction options can be beneficially combined with enhanced dewatering and/or drying to further reduce the quantity of sludge disposed and to increase net cost savings.

TABLE 46. ECONOMIC ANALYSIS OF MOS-LLX AND USE OF A STOICHIOMETRIC AMOUNT OF FERROUS SULFATE FOR Cr^{VI} REDUCTION AT IWTP PLANT #2 AT WR-ALC.

Treatment Method,	Cr reduction	Stoich. FeS Plant 2	Current Plant 1
	Metal removal	LLX-MOS Plant 2	Current Plant 1
	Sludge treatment	Current	
Operating Schedule	Hrs/year 8,064	Electricity, cent/kWh	3.785
Hrs/shift 8	Shifts 3	Waste disposal cost, \$/lb	0.22
Days/week 7	Reduction of Sludge Quantity	370 ton/year	
Weeks/year 48	for Disposal	63 Percent	
PLANT CAPACITY	Flowrate, gal/day		100,000
CAPITAL COST			
Purchased Equipment Cost (PEC)			\$ 30,003
	Basis	Percentage	
Installation	PEC	40%	\$ 12,001
Instrumentation	PEC	20%	\$ 6,001
Piping	PEC	25%	\$ 7,501
Electrical	PEC	15%	\$ 4,500
Engineering	PEC	30%	\$ 9,001
Contingency	PEC	50%	\$ 15,002
Fixed Capital Investment (FCI)	\$ (1996, installed)		\$ 84,009
OPERATING COST, \$/yr			
	Basis	Percentage	
Materials			\$ -
Maintenance,	Estimate		\$ 455
Operating Supplies	Estimate		\$ 10,897
Electricity			
Operating labor			\$ 5,103
Supervision,	labor	20%	\$ 1,021
Laboratory charges,	labor	15%	\$ 765
Plant overhead costs	labor +supervision	60%	\$ 3,947
	+maintenance		
Total operating cost			\$ 22,188
COST SAVINGS, \$/yr			
Savings in waste disposal cost			\$ 162,677
Net cost savings			\$ 140,488
PAYBACK PERIOD, yr			0.6

**TABLE 47. ECONOMIC ANALYSIS OF USING A THEORETICAL AMOUNT
OF FERROUS SULFATE FOR Cr^{VI} REDUCTION AND BORAX-
ASSISTED SLUDGE BLANKET FOR METAL REMOVAL AT
OC-ALC IWTP.**

Treatment Method,	Cr reduction	Stoichiometric FeSO ₄
	Metal removal	Impurity built SCC blanket
	Sludge treatment	Current
Operating Schedule	Hrs/year 8,064	Electricity, cent/kWh 3.785
Hrs/shift 8	Shifts 3	Waste disposal cost, \$/lb 0.14 dry/ 0.18 wet
Days/week 7	Reduction of Sludge Quantity 344 ton/year	
Weeks/year 48	for Disposal 22 Percent	
PLANT CAPACITY	Flow rate, gal/day	900,000
CAPITAL COST		
Purchased Equipment Cost for added Instrumentation (PEC)		\$ 48,921
Installation		\$ -
Instrumentation		\$ 48,921
Piping		\$ -
Electrical		\$ -
Engineering		\$ -
Contingency		\$ -
Fixed Capital Investment (FCI) \$ (1996, installed)		\$ 48,921
OPERATING COST, \$/yr		
	Basis	Percentage
Materials		\$ 51,974
Maintenance,	FCI	6% \$ 2,935
Operating Supplies	maintenance	15% \$ 440
Operating labor		\$ 2,880
Supervision,	labor	20% \$ 576
Laboratory charges,	labor	15% \$ 432
Plant overhead costs	labor +supervision +maintenance	60% \$ 3,835
Total operating cost		\$ 63,072
COST SAVINGS, \$/yr		
Savings in waste disposal cost		\$ 123,959
Net cost savings		\$ 60,887
PAYBACK PERIOD, yr		0.8

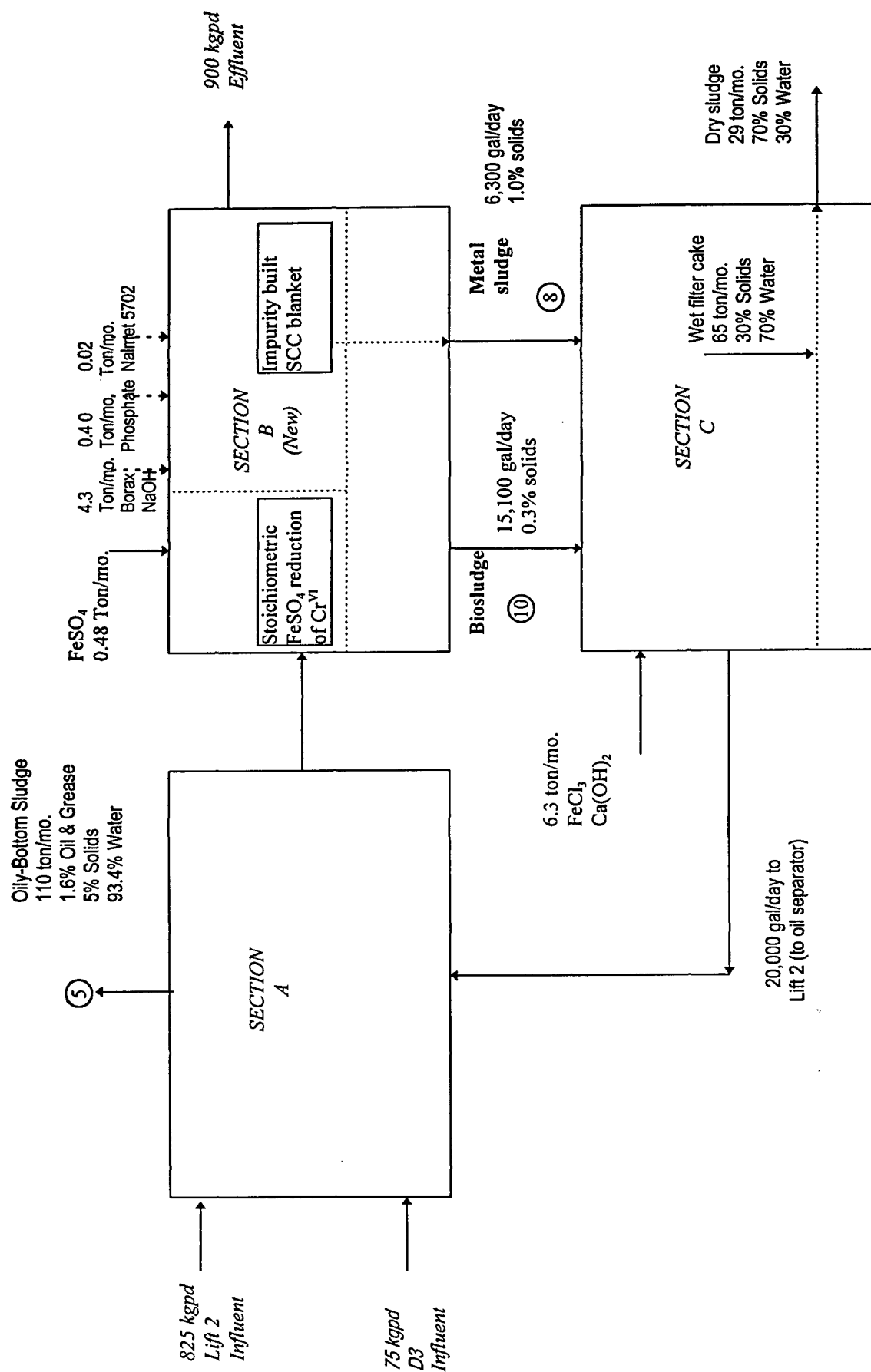


Figure 31. Effect of Application of Stoichiometric Ferrous Sulfate Chrome Reduction and Borax Assisted Impurity Built SCC Blanket on Process Flows at OC-ALC IWTP.

TABLE 48. SUMMARY OF ECONOMIC ANALYSIS FOR ALTERNATIVE METAL REDUCTION OPTIONS.

AF-ALC Site/Plant	Technology	Sludge Quantity Eliminated		Baseline Waste Disposal Cost (\$/yr)	Net Annual Savings (\$)	Installed Capital Cost (\$)	Simple Payback (years)
		tons/yr	Weight Reduction (%)				
WR-ALC IWTP Plant #1 and #2	Reduced FeSO ₄ use and improved Sludge Blanket	438	75	257,000	176,700	32,900	0.2
WR-ALC IWTP Plant #2	Reduced FeSO ₄ use and Mixing/Oil Skimming (MOS) LLX	370	63	257,000	140,500	84,000	0.6
WR-ALC IWTP Plant #2	Chrome LIX	273	47	257,000	101,200	84,000	0.8
WR-ALC IWTP Plant #2	Chrome LIX and MOS LLX	380	65	257,000	126,800	168,000	1.3
OC-ALC	Reduced FeSO ₄ use and improved Sludge Blanket	344	22	617,800	60,900	48,900	0.8
OC-ALC Stream D3	Chrome LIX	73	5	617,800	7,200	84,000	11.6
OC-ALC Stream D3	Reduced FeSO ₄ use and MOS-LLX	212	13	617,800	57,200	84,000	1.5
OC-ALC Stream D3	Chrome LIX and MOS LLX	215	13	617,800	39,100	168,000	4.3

H. CONCLUSIONS AND RECOMMENDATIONS FOR METAL REDUCTION

The laboratory results and economic analyses indicate that three concepts -- borax-assisted improved sludge blanket for metal precipitation/removal, A-LIX for Cr^{VI} removal, and MOS-LLX for metals removal -- are technoeconomically feasible. Among these three concepts, the A-LIX and MOS-LLX are more economical if employed to streams with the highest impurity levels (i.e., Stream D3 for OC-ALC and IWTP Plant #2 for WR-ALC). It is recommended that all of the concepts be tested in the field to identify the most practical process options.

Based on the stream analyses (Section IV), the recommended test sites are as follows:

- Improved sludge blanket: OC-ALC (to treat entire IWTP flow)
- A-LIX process: WR-ALC (IWTP Plant #2; plating shop effluent)
- MOS-LLX process: WR-ALC (IWTP Plant #2; plating shop effluent)

The pilot unit for both A-LIX and MOS-LLX processes will be the same. As such, both processes can be easily tested. This testing will provide data on how flexible the processes are with respect to stream composition.

SECTION VII

BIOSLUDGE REDUCTION AND ELIMINATION

A. INTRODUCTION AND BACKGROUND

1. Scope of Biosludge Problem

Biosludge is a significant problem at OC-ALC where it introduces approximately one third of the total solids in the thickened sludge stream IWTP#11. Biosludge is composed of bacterial matter, both live and dead. The bacterial cell walls keep water inside the cell; waste activated sludge bacteria contain 90 percent water. The cell membranes are sensitive to shear, to heat, and to harsh chemicals, but the shear produced in pumping and in pressure filtration is not sufficient to cause cell membrane breakdown. The dewatering of biosludge is accomplished by three general methods^(6-8,12,31,32): (a) drying in large shallow pools; (b) chemical conditioning by ferric chloride and lime followed by filter pressing; and (c) flocculation followed by belt presses. The belt press is capable of dewatering the biosludge by its shearing action, but is not recommended for intermediate quantities such as those produced at the AF-ALCs because of the high cost of small sized belt presses. Drying in shallow pools is not suited to AF-ALC sludges because of safety, odor and VOC emission problems as well as land costs. Ferric chloride and lime conditioning is the most common treatment method for waste activated sludge because of the ease of filtration and the reliability of the treatment. Wet biomass in OC-ALC sludge IWTP#11 is about 33 percent of the overall mass, or about 60 tons/month. The planned upgrade of WR-ALC IWTP plant #1 includes installation of a biotreatment facility that will generate approximately 90 tons/year of biosolids which may be thickened to 6 percent solids. When treated with ferric chloride and lime followed by pressure filtration, this will produce over 500 tons/year of filter cake that will be disposed of at an estimated annual cost of \$230,000.

B. BIOSLUDGE DESTRUCTION TECHNOLOGIES PROJECT FOR OC-ALC

The Oklahoma City Air Logistics Center (OC-ALC) at Tinker AFB currently pays a high cost for disposal of the biosludge produced at their IWTP. The OC-ALC, therefore, contracted

Battelle to conduct a project on "Acid/Heat Treatment Technologies For Biosludge". The objective of this OC-ALC project is to identify, develop and demonstrate a suitable technology to reduce biosludge disposal costs at the IWTP at OC-ALC, while maintaining its performance. The selection of candidate technologies for laboratory feasibility/optimization experiments were based on the work performed in Task I-2, I-4, and I-5 of this AL/Envionics project. The best processes determined by their technical merit and economic viability were further tested in the laboratory with the objective of selecting the best process for scale up and field demonstration. The effort leading to the selection of candidate technologies for feasibility/optimization testing were reported earlier⁽³⁾ and are summarized here.

The OC-ALC IWTP operations were analyzed to characterize the flow and treatment of various streams that either contribute to or contain sludges especially biosludges. The streams were identified, sampled and analyzed. Literature on current commercial technologies was investigated. Biosludge reduction by dewatering and by thermochemical means also were briefly tested at the laboratory, batch scale and evaluated for their technological and economic viability.

Comparison of the volume reductions possible through the use of these technologies on different sludges is given in Table 49. The volume reduction anticipated is in comparison with the overall quantity of sludge currently being disposed (IWTP #5, unfiltered IWTP #11 and filter cakes from filtration of IWTP #11). The values in parentheses are for the particular stream. The data presented are based on filtration of the sludges to cakes with solids content of 25 percent. The drying level achievable with high organic content was assumed to be 70 percent solids, and that of inorganic solids were taken as 90 percent. Additional data for the processes indicate that an 85 percent to 90 percent volume reduction is achievable by acid hydrolysis and wet air oxidation, when they are applied to OC-ALC sludge IWTP #11.

TABLE 49. COMPARISON OF VOLUME REDUCTION POTENTIAL FOR THE DIFFERENT TECHNOLOGIES AND TREATMENT OPTIONS.

Technology	Target Streams	Volume reduction anticipated		Years till required to demonstrate
		Filtered only	Dried	
Acid hydrolysis	IWTP#11	53%	87%	1.5
Wet Air Oxidation SCWO	IWTP#11	78%	94%	1.5
	IWTP#11 + IWTP#5	85%	96%	2
Drying	IWTP#11 + IWTP#5		88%	1

The economic analysis of the thermochemical biosludge elimination technologies was performed for various treatment strategies including integration of IWTP #5 treatment into the process and the separate treatment of IWTP #10 as opposed to just IWTP #11. Treatment of IWTP#5 by filtration and drying contributed a significant portion of the potential savings achieved by combined treatment of IWTP #5 and other sludges. Since treatment of IWTP #5 is not of concern for this project, the economic effects of its treatment have been taken out of the analysis presented in Table 50, and only the treatment of IWTP #11 is presented. The treatment of IWTP #10 alone was not economical compared to treatment of IWTP #11. Of the processes evaluated, the application of acid hydrolysis and wet air oxidation were the most promising technologies within the limits of the capital budget for the application of the chosen technologies. Payback periods were 1.7 for acid hydrolysis and 3.7 years for wet air oxidation. Methodology for eco-nomic analysis was based on EPA recommended practice and standard industry practice^(12,24-26).

It should be noted that the drying option had a reasonable payback, but during subsequent investigations in Task I-5 of the project, the fluid-like consistency of the sludge was considered by dryer manufacturers to be a serious problem.

TABLE 50. CAPITAL COST AND PAYBACK PERIODS FOR APPLICATION OF THERMOCHEMICAL TECHNOLOGIES.

Process:	Ranking for IWTP#11 Treatment		
	Capital Cost	Payback Period (years)	Ranking ^(b)
Wet air oxidation	\$ 420,000	3.7	3
Supercritical water oxidation	\$1,140,000	26	5
Acid hydrolysis ^(a)	\$ 380,000	1.7	1
Anaerobic digestion	\$ 750,000	2	4
Drying	\$ 540,000	1.8	2

^(a) It should be noted that the capital cost and payback for acid hydrolysis include a 50% contingency because the process is not fully developed commercially and may require the addition of unknown auxiliary equipment in its application. These have already been determined for the mature technologies, and were included in their costing.

^(b) Based on assigning equal weights to ranking by capital cost and payback period.

C. EXPERIMENTAL EVALUATION OF BIOSOLIDS REDUCTION TECHNOLOGIES

The technology assessment included the evaluation of the effectiveness of wet air oxidation, acid hydrolysis, supercritical water oxidation, Thermal Environmental Energy Systems (TEES®), and drying with a hollow flight dryer. All of the thermochemical technologies investigated were effective in reducing the biosolids waste. Furthermore, the work revealed that the major cost savings can be achieved when oily bottoms sludge and the thickener sludge are treated in tandem. Enhanced filterability of the thermally treated sludges and removal of biosludge from the load on the current filter presses provides most of the benefits of treatment. The technically feasible technologies were compared on the basis of capital and operating costs.

1. Acid Hydrolysis

Hydrolysis is the chemical reaction in which a compound reacts with water. Many organic materials can be broken down to smaller molecules by hydrolysis. Acid hydrolysis has been used extensively for the pretreatment of cellulosic biomass prior to fermentation. The use of acid hydrolysis to treat biosludge from sewage treatment plants has been reported in the

literature⁽³²⁻³⁸⁾. The term acid hydrolysis was initially used in describing acid-catalyzed hydrolysis, whereas in practical application the process involves partial oxidation as well as hydrolysis processes, so some solid organic material is solubilized and a smaller portion is oxidized into carbon dioxide, nitrous oxide and nitrogen. The liquid-phase product contains solubilized organic material and unreacted (mostly inorganic) solids that must be treated⁽³²⁻³⁸⁾.

This study included an initial investigation of two acid hydrolysis systems. One is the recently developed Pacific Northwest National Laboratory (PNNL) process using nitric acid. The other was developed by Dow Chemical GMBH of Germany in the late eighties. The Dow process was tested on a pilot scale with sulfuric acid, but the full scale process was designed for use with hydrochloric acid in order to avoid the discharge of sulfates in the final effluent stream. Both methods require a pH of approximately 1 in the incoming stream for proper hydrolysis. Overall, a 90 percent reduction in the volume of biosludge has been claimed for previous industrial operations.

In the Dow process sludge is acidified then heated and enters the hydrolysis reactor. The reactor operates at about 150 C and 5 atm. to 180 C and 9 atm.. The reactor is a simple plug-flow, tubular reactor constructed of stainless steel. Some off-gas containing CO₂, N₂, and N₂O is produced. After leaving the bioreactor, inorganic solids can be easily separated from the hydrolyzed stream. Depending on the nature of the biotreatment process and the waste water stream, the hydrolyzed recycle stream may or may not have to be neutralized prior to returning to the bioreactor. Results of Dow Chemical Company continuous acid hydrolysis system integrated with a biotreatment process show that 98 percent of BOD in the hydrolysis effluent is digested under ideal conditions. Also a surprisingly high 88 percent of COD and 86 percent of TOC in the hydrolyzate are digested by the biotreatment stage. Operating conditions for the Dow process are one and a half to two hour holding times at 150 C under 4.0 to 5.5 Bar pressure at pH 0.5 to 1.0. The major stumbling block for the application of this technique on mixed sludges is the low pH, that may cause the metal precipitates to return to solution. Dow's results indicate that a significant portion of the metals are dissolved back into solution, but the majority of the analyzed metals remains in solid form^(33,34).

In the current investigation by PNNL, effective solubilization was 60-70 percent of the organic solids in the thickened sludge and 87 percent in the dilute biosludge. The heat treatment allows easy removal of the remaining organic solids and inorganic solids from the hydrolyzed waste water stream. Previous bench-scale tests at PNNL also indicated that the hydrolysis product was amenable to further biotreatment. Battelle has tested sludge streams IWTP#10 and IWTP#11 for effective treatment by acid hydrolysis, wet air oxidation, and TEES. These share the need for elevated pressure tanks that are resistant to oxidation. The tests discussed below were done at PNNL and have shown the technical feasibility of applying their acid hydrolysis to the biosludge stream.

Tests were performed at temperatures ranging from 120°C to 180°C and pressures ranging from approximately 150 psig. For each batch test, a weighed quantity of sludge sample, approximately 250 mL, was placed in the 1-L batch autoclave reactor with 1000 psi inert gas. Next the autoclave reactor was vented to approximately 100 psig and heated to the designated temperature. Upon cooling, the autoclave reactor was depressurized, and the liquid and gas contents were measured and analyzed. Nitric acid or sulfuric acid were added to IWTP#11 to a concentrations of 3.8 and 2.9 weight percent respectively (maintaining a nitric acid/biosludge solids weight ratio of 0.5 to 1) and heated to 180°C for 5 minutes.

Total suspended solids in the nitric acid treated sludge were decreased by approximately 46 percent and the volatile suspended solids were decreased by approximately 51 percent by this treatment, indicating at least 60 percent biosludge solubilization and up to complete digestion. Sulfuric acid treatment resulted in total suspended solids (TSS) reduction by approximately 57 percent and the volatile suspended solids reduction by approximately 57 percent indicating a high degree of biosolids solubilization. A similar test on the pure biosludge stream IWTP#10 resulted in TSS and volatile suspended solids content decrease by approximately 87 percent.

Filtration tests were conducted on IWTP#11 samples and product samples to evaluate the effect of treatment on dewaterability of the treated sludge. The 10 minute vacuum filtration tests were conducted on 100 gram samples through a Whatman #4 filter. Acid treatment allowed for better dewatering of the solids that remained after treatment. Untreated IWTP #11

filter cakes contained 13.9 percent solids and the treated IWTP #11 filter cake contained 28.8 percent solids in nitric acid tests and 38.6 percent solids in the sulfuric acid test, doubling and tripling the solids content achievable in filtration of IWTP #11.

The filtrate analyses of both tests shows the chemical oxygen demand of the product filtrate is significantly higher than that of the feed, indicating biosolids solubilization. The filtrate was also analyzed for iron and chromium, which are two of the major metal species present in IWTP #11 in order to estimate the quantity of metal species solubilized by the acid treatment. Approximately 7 percent of the total iron and less than 0.05 percent of the total chromium was solubilized by nitric acid treatment. However, approximately 67 percent of the iron and 0.4 percent of the chromium was present in soluble form after the sulfuric acid treatment.

The major gas products of the nitric acid tests were CO_2 , N_2 , and N_2O and a significant amount of CO and other nitrogen oxide gasses, indicating nitrate consumption. The total gas yield during the nitric acid reaction was approximately 9 (standard conditions) whereas the sulfuric acid test yielded 1.6 liters product gas/liter of liquid feed. The sulfuric acid test did not show sulfate consumption in that little CO_2 and CO were found in the product gas and the major gas product was nitrous oxide.

2. Wet Air Oxidation

US Filter/Zimpro, Inc. (Rothschild, Wisconsin) developed wet air oxidation (WAO) for the thermochemical oxidation of organics (at concentrations of 2-20 percent) and other hazardous wastes in aqueous streams. WAO is carried out at elevated temperatures of 275 C to 320 C and high pressures of 40 to 120 atm (about 600 to 2,000 psig). Compressed air is the usual source of the oxygen. Commercial WAO systems are continuous flow vertically-oriented cylindrical reactors that can be used to oxidize a variety of components in industrial waste waters and sludges as part of an overall waste water treatment process. In this process compressed air is added to the pressurized waste stream and the mixture is heated using a heat exchanger to supply additional heat, if required. After heating, the waste water flows through a reactor where the waste constituents react with oxygen. For most organics, 99.5 percent destruction of the compound can be obtained within residence times 30 - 60 minutes at 275 C. The reactor effluent

is cooled and then discharged through a pressure control valve into a separator where the off-gas is separated from the liquid effluent. WAO is commercially available in typical units for treatment of 5 gpm to 70 gpm^(3,12,39-45).

Battelle tested WAO in order to evaluate the viability of WAO treatment of mixed and unmixed biosludge. The test was conducted using a setup similar to that for acid hydrolysis. The tests of IWTP#11 were performed on 25 gram samples combined with 225 grams of distilled water in an autoclave with air added to a pressure of 350 psig (approximately 10 to 20 percent excess air, based on the chemical oxygen demand of the IWTP#11 sludge). The reactor was then heated to 300°C, reaching a pressure of 2000 psig, and was held at that temperature and pressure for 1 hour.

Approximately 62-70 percent of the total suspended solids and volatile suspended solids were solubilized in the test of WAO, slightly higher conversion than acid hydrolysis tests. The chemical oxygen demand of the composite product was significantly lower than that of the feed and the majority of the COD was solubilized in the filtrate. No chromium or iron was solubilized in treatment with wet air oxidation. The gaseous products were CO₂, CO, and CH₄ (on a N₂ and O₂ free basis). The reaction gas yield (N₂ and O₂ free basis) was 84 liters product gas (standard conditions)/liter of sludge feed. The total gas yield including N₂ and O₂ was 574 liters/liter of sludge, and comparable to the reactor charge (approximately 667 L air (standard conditions)/L sludge that were added to the reactor). Thus there was no net increase of gas flow as the reaction progressed. The tests indicate that wet air oxidation results in the complete breakdown of a much larger percentage of the organics as compared to acid treatment, however, sufficient solubilized organics remain to require further treatment of the product filtrate by its return to the biotreatment facility. Filtration tests were conducted on the WAO reaction product to evaluate the effect of WAO on the dewatering of the remaining product sludge. After treatment the filter cake solids content was 28.7 percent.

3. Supercritical Water Oxidation

Supercritical Water Oxidation (SCWO) is the oxidation of organic compounds with air or oxygen in the presence of a high concentration of water at temperatures and pressures

above the critical point of water (374°C and 218 atm). In practice, SCWO is usually carried out at 400 C to 650 C and 250 atm to 400 atm. The sludge or waste is pressurized, preheated, and mixed with the oxidant, usually compressed air. The mixture enters a tubular plug-flow reactor where the oxidation takes place. The reactor effluent passes through a series of separators and pressure let-down valves. Inorganic salts which are originally present in the feed or formed in the reactor are generally not soluble in supercritical water and precipitate out of the fluid phase. The off-gas consists primarily of CO₂ and water vapor. SCWO operates most effectively on wastes containing 1-20 percent organic material in water. Typical destruction efficiencies for most organics are greater than 99 percent at 400-500 C and 1-5 minute residence times. Similar destruction efficiencies can be achieved with residence times of less than a minute at higher temperatures. Primary technical difficulties are the high-pressure and temperature and the alloy construction required to protect against corrosion. These lead to a high capital cost. Handling of inorganic solids is also an issue and can reduce reliability⁽⁴⁴⁻⁵³⁾.

The process was not tested for the OC-ALC biosludge destruction project, but a technical evaluation and determination of operating conditions was conducted using the available literature. In the technical evaluation SCWO was found to be an effective process for destruction of over 99 percent of the organic volatile matter in the sludge, and the expected solids concentrations achievable in filter cakes (pressure filtration) may be estimated at better than 30 percent based on vacuum filtration behavior of the sludge treated by WAO. Because of its high capital cost and energy requirements, it was evaluated predominantly as a treatment for the combination of IWTP#11 sludge with filter cakes from pressure filtration of IWTP#5. Application of SCWO to any of the sludge streams alone was expected to be overly expensive. No metal resolubilization problems were expected because the process does not use acids.

4. Thermochemical Environmental Energy System®

The Thermochemical Environmental Energy System (TEES®) was developed as an alternative to wet air oxidation (WAO) and supercritical water oxidation (SCWO) for the treatment of aqueous waste streams containing organics. Like WAO and SCWO, TEES® is a high temperature and pressure thermochemical process operating at temperatures from 300 C to

350 C and pressures from about 150 atm (2200 psig) to 200 atm (3000 psig)⁽³⁾. Unlike WAO and SCWO, TEES® does not use oxygen to oxidize the organics. A supported nickel and/or ruthenium catalyst promotes the reaction of organics with water to produce only CH₄ and CO₂.

The waste stream is pressurized and passes through a heat recovery system and a preheater, and flows through a tubular reactor packed with catalyst pellets. The reactor effluent passes through a heat exchanger and then depressured into a separator where the off-gas is separated from the clean liquid effluent. Typically, the off-gas contains about 55 percent CH₄, 40 percent CO₂, and 5 percent H₂ and other hydrocarbon gases. The gas has a heating value of 600 btu/scf and can be used as a replacement for natural gas in many applications. Typical residence time in the catalytic reactor is 5 minutes to 1 hour and typical conversion efficiencies are 95 to 99 percent for most organics. The effective catalysis of the reaction to produce methane eliminates the need for the addition of air or oxygen to the reactor, thus avoiding the cost of providing compressed air or oxygen. TEES® was originally developed to convert high-moisture biomass to energy. It has been applied to food processing sludges and has been tested on biosludge. In recent batch reactor tests with an industrial waste water treating biosludge, organic destruction, as measured by the decrease in chemical oxygen demand (COD), was greater than 96 percent at 350 C. Current development efforts have been focused on industrial waste waters such as nylon manufacturing waste water, polyol waste water, and olive processing waste water. Organic destruction (measured by decrease in COD) for these tests was generally greater than 95 percent.

Preliminary testing of TEES® technology on OC-ALC sludge IWTP#11 was performed by Battelle to evaluate the effectiveness of the TEES® process for treating biosludge. In this test, approximately 35g of TEES® catalyst was added to 250g of IWTP#11. The solution + catalyst were then placed in an autoclave similar to that used for acid hydrolysis experiments, and heated to 350°C (3000 psig) and held there for 1 hour. Reaction product gas had CO₂ and CH₄ in the approximate proportions expected from TEES®. Approximately 94.6 percent of the COD from the feed was removed but when the product solution settled overnight, an organic liquid phase formed. These results indicate that the TEES® catalyst was effective in partially breaking down the biosludge and other insoluble organics. However, the high proportion of hydrogen and organic liquid produced in the reaction relative to methane generation indicate that

the catalyst was "poisoned". The "poisoning" was attributed to the inorganic constituents of IWTP#11 such as sulfates. TEES® is expected to be more effective in treating a pure biosludge such as IWTP#10 that has a minimal amount of inorganics present, but the quantities of dissolved sulfates in the sludge are still a matter of concern.

D. LABORATORY FEASIBILITY/ OPTIMIZATION TESTS

The two most promising technologies found in the technical evaluations were wet air oxidation and acid hydrolysis. Additional experiments were conducted at Battelle (acid hydrolysis) and Zimpro (wet air oxidation) to determine the optimal operating conditions for the processes. The main optimization criterion was the solids content of the filter cakes. The tests were performed as part of the Biosludge treatment project for OC-ALC. The results are reported in Appendix G.

SECTION VIII

CONCLUSIONS

The following conclusions can be drawn from this research and development project.

- (1) All AF-ALC IWTPs could potentially benefit from availability of more effective technologies for reducing the quantity (volume or mass) of metal hydroxide and organic-type (oily and/or biosolid) sludges. The previous opportunities to achieve this quantity reduction was through enhanced dewatering/drying since the majority of the sludge mass is water. Additional key opportunities existed for reducing the mass of sludge solids, and therefore, the sludge quantity, by changing IWTP processes.
- (2) A detailed characterization of three AF-ALC IWTP sites and their sludges indicated that the majority of the sludge solids are additives used to remove metals and to satisfactorily filter the sludge so alternative technologies offer some reduction potential.
- (3) The use of polymer flocculants to completely eliminate the addition of lime was demonstrated for WR-ALC sludges. For OC-ALC, the ferric chloride and lime addition could be reduced by more than 50 percent by segregating the metal hydroxide sludge from biosludge and flocculating the metal hydroxide sludge with polymers. Both of these technology options were economical as shown in Table 51.
- (4) The use of a low-humidity (low-temperature) dryer was successfully demonstrated at Tooele Army Depot/OO-ALC. The process was found to be economical (Table 51). Application to WR-ALC appears to be technoeconomically feasible.

TABLE 51. COST SUMMARY FOR ALTERNATIVE IWTP PROCESSES PROPOSED.

AF-ALC Site/Plant	Technology	Sludge Quantity Eliminated		Baseline Waste Disposal Cost (\$/yr)	Net Annual Savings (\$)	Installed Capital Cost (\$)	Simple Payback (years)
		tons/yr	Weight Reduction (%)				
Flocculation/Dewatering							
WR-ALC IWTP #17	Polymer Flocculation	92	16	257,000	31,700	64,400	2.0
OC-ALC IWTP #8 and #10	Polymer Flocculation	1,209	75	617,800	450,300	222,700	0.5
Drying							
OO-ALC	Low humidity drying	41	32	163,300	120,000	116,200	1.0
WR-ALC	Low humidity drying	358	61	257,000	108,200	348,500	3.2
Metal Reduction							
WR-ALC IWTP Plant #1 and #2	Reduced FeSO ₄ use and improved Sludge Blanket	438	75	257,000	176,700	32,900	0.2
WR-ALC IWTP Plant #2	Reduced FeSO ₄ use and Mixing/Oil Skimming (MOS) LLX	370	63	257,000	140,500	84,000	0.6
WR-ALC IWTP Plant #2	Chrome A-LIX	273	47	257,000	101,200	84,000	0.8
WR-ALC IWTP Plant #2	Chrome A-LIX and MOS LLX	380	65	257,000	126,800	168,000	1.3
OC-ALC	Reduced FeSO ₄ use and improved Sludge Blanket	344	22	617,800	60,900	48,900	0.8
OC-ALC Stream D3	Chrome A-LIX	73	5	617,800	7,200	84,000	11.6
OC-ALC Stream D3	Reduced FeSO ₄ use and MOS-LLX	212	13	617,800	57,200	84,000	1.5
OC-ALC Stream D3	Chrome A-LIX and MOS LLX	215	13	617,800	39,100	168,000	4.3

- (5) Several viable metal separation chemistries to avoid use of an excess of iron compounds were demonstrated on synthetic and spiked IWTP samples. Liquid-liquid extraction technique is specially attractive, but a significant opportunity exists to improve the currently used hydroxide precipitation process.
- (6) Use of acid hydrolysis and wet air oxidation to reduce the amount of biosolids as well as to more effectively dewater the sludge were found to be technically feasible. A volume (mass) reduction of 80 percent is economically feasible.

SECTION IX

RECOMMENDATIONS

A. RECOMMENDATIONS FOR PHASE II

The following technologies are proposed for field demonstration at various AF-ALCs based on potential for sludge volume reduction and payback criteria. Additional rationale for testing are provided below:

1. Flocculation/Dewatering

Since dewatering is the largest single need and since enhanced dewatering has a positive impact even if source reduction reduces the amount of suspended metal hydroxide and biosludge solids it is given the highest priority for testing. The two demonstrations proposed are:

- (1A) WR-ALC -- The WR-ALC IWTP produces a large amount of metal hydroxide sludge using an excessive amount of lime. The use of polymers can potentially eliminate the use of lime. The proposed field test data can be used immediately by WR-ALC to implement the process as they are in the midst of an IWTP upgrade.
- (1B) OC-ALC -- The OC-ALC IWTP produces more sludge than WR-ALC, but the OC-ALC sludge is different in its dewatering behavior because of the presence of biosludge. The proposed scheme to dewater this sludge is to use polymers to flocculate the metal hydroxide sludge and use the conventional ferric chloride and lime conditioning for biosludge and then dewater these two treated sludges. This scheme will serve as a benchmark for the thermal conditioning/treatment technology selected in Item 4 below. The results on dewatering of the mixed sludge will be pertinent for future operations at WR-ALC when they install a biotreatment facility.

2. Metal Separation

The OC-ALC, WR-ALC, and SA-ALC IWTPs use large amounts of iron compounds to reduce Cr^{VI} and RCRA metals. It is proposed that two alternate technologies be tested at OC-ALC or WR-ALC to reduce the amount of iron compounds used and thus achieve source reduction. The two technologies proposed can not only benefit the Air Force, but also other DoD and industrial facilities.

- (2A) The use of mixing/oil skimming (MOS) technology to remove RCRA metals in conjunction with use of a theoretical amount of FeSO_4 to reduce Cr^{VI} is proposed. A pilot plant for the MOS, a liquid-liquid extraction technique, is already available from a previous Environics project. A benchmark for evaluating this technology should be the use of an SCC sludge blanket made out of the impurities in the feed waste water.
- (2B) After successful demonstration of 2A, the metal separation technology can be further advanced by replacing FeSO_4 treatment with liquid ion exchange to remove Cr^{VI} . The MOS pilot plant can be modified for this additional testing.

3. Drying

While thermal drying can be a cost effective means to further reduce the cost of sludge disposal, its impact is expected to be less than through enhanced dewatering and source reduction through alternate methods to remove metals. However, drying can be a higher priority if dewatering and source reduction are unsuccessful or if the currently used drying systems need to be improved as in the case proposed below.

- (3A) OO-ALC -- The dewatered sludge at OO-ALC is quite oily and causes undesirable air emissions from the current dryer. The emissions can be eliminated with low-humidity drying (a JWI system). The Phase I pilot tests were successful and the data were used by OO-ALC to specify a full-scale system. It is recommended that the full-scale system performance be documented and economics re-evaluated based on testing at OO-ALC.

This drying system could be the system of choice for future IWTP upgrades at OC-ALC and WR-ALC.

4. Biosludge Reduction

Biosludge dewatering is a major problem for a large number of IWTPs across various industries and for municipalities. It is a major problem for OC-ALC and a current problem at SA-ALC. Also, WR-ALC is likely to encounter this problem in the near future. Therefore, treatment of biosludge to alter its dewatering behavior and its suspended solids content is recommended based on Phase I results. However, a separate program already funded by OC-ALC is the proposed program for demonstrating the preferred technologies, i.e., acid hydrolysis and wet air oxidation/thermal conditioning.

In recommending the above technologies, a number of other technologies were eliminated from consideration. Examples of the technologies not recommended are: (1) polymer flocculation of mixed sludge; (2) use of LLX for removal of Cr^{VI} alone; (3) conventional drying technologies that cause potential air emission problems such as fluid bed and flash dryers.

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APPENDIX A

**ANALYTICAL METHODS FOR IWTP
STREAM CHARACTERIZATION**

APPENDIX A
ANALYTICAL METHODS FOR IWTP
STREAM CHARACTERIZATION

The analytical methods described in Section IV-B are used for the analysis of particular sludge properties. The following list associates the sludge component with the test methodology used to determine its quantity:

- (a) Oil and organic contaminants:
Fat, oil and grease (FOG), Volatile solids, COD, TOC, Elemental Carbon
- (b) Metal contaminant concentrations (by atomic absorption)
- (c) Hexavalent chromium (colorimetry)
- (d) Concentrations of phenol and its derivatives (colorimetric test)
- (e) Solids content:
Total residue, TSS, ash content (fixed solids).

The analytical methods used to detect each type of contaminant are provided below. Each material is detected by a number of methods.

- (1) Biosolids are detectable in the following analytical tests. These tests are not specific for biosolids since they detect materials other than biosolids alone.
 - (a) Volatiles
 - (b) TOC
 - (c) Elemental carbon
 - (d) Total solids (residue).
- (2) Oil and grease tests are specific for oils and heavy fuel but are not capable of detection of light fuels and solvents. The rest of the tests on this list are not specific for fuel, oil and grease. TOC and elemental carbon tests detect solvents

and light fuels as well as other organics not detected in the FOG or tests for solids.

- (a) Fat, Oil and grease (FOG)
 - (b) TOC
 - (c) Elemental carbon
 - (d) Partially in total solids.
- (3) Solvents and fuel:
- (a) TOC
 - (b) Elemental carbon.
- (4) Inorganic material (metals):
- (a) Metal analysis by atomic absorption (AA)
 - (b) Total solids
 - (c) Ash.
- (5) Hexavalent chrome is detected by the following tests:
- (a) Hexavalent chrome (colorimetric test specific to hexavalent chromium)
 - (b) Chrome metal analysis by atomic absorption
 - (c) Ash
 - (d) Total solids.

TABLE A-1. CHARACTERIZATION OF PROCESS AND IWTP STREAMS.

Analysis	APHA Test	EPA Method
BOD (5 day)		405.1
COD (ppm)		410.7
Nitrate/Nitrite		300.0
Sulfate		300.0
Chloride		300.0
pH		150.1 at site
Hexavalent chromium	3500-Cr D	7196
Silicon	3120-Si B	
Calcium		200.7/215.1
Iron		200.7/236.2
Aluminum		200.7/202.1
Chromium		200.7/218.2
Lead		200.7/239.2
Nickel		200.7/249.2
Cadmium		200.7/213.2
Copper		200.7/220.2
Zinc		200.7/289.1
Fixed solids (Ash)	-2540 E	
Total volatiles	-2540	
TSS	-2540	
Total Dissolved Solids	-2540	
Total Residue	-2540 B or G	160.2
Oils and grease		413.1
TOC	5310 B	
C		ASTM D5291/Standard
H		ASTM D5291/Standard
N		ASTM D5291/Standard
S		ASTM D5291/Standard
Phenol		420.1
Zeta potential	Special test	

APPENDIX B

**RESULTS OF ANALYSIS OF IWTP
SLUDGES AND STREAMS**

APPENDIX B

RESULTS OF ANALYSIS OF IWTP SLUDGES AND STREAMS

The following tables contain the results of the sludge and IWTP stream analysis conducted at OC-ALC, WR-ALC and OO-ALC. These results are discussed in Section IV-B. The analytical techniques for each test are specified in Appendix A. Additional analytical test data from IWTP and environmental management log books was used and is not provided in this Appendix because of its great bulk.

TABLE B-1. RESULTS OF SLUDGE STREAM ANALYSIS AT OC-ALC.

Stream no.	Stream description	BOD (5 day)	COD (ppm)	Filtered fraction COD	COD calc. from Total Volatiles (48 to 14)	COD contribution of metals	Nitrate/Nitrite	Sulfate	Chloride	pH	pH of filtrate	Silicon	Calcium
IWTP 1b	D1/D2 Effluent (D3 effluent)	1600	3375	---1766	1701								
IWTP 2	Lift #2 Influent	160	64							7.94			
IWTP 2	Lift #2 Influent (tests for EPA filing)		578										
IWTP 4	D3 Sludge (paint stripping)	6000	3360										
IWTP 5	Oil Separator Sludge		11955		61714							Barium	3
IWTP 5	Oil Separator Sludge TCLP extracted									8			
IWTP 6	Oil Separator Effluent		421							7.53			
IWTP 7	Equalization Basin Effluent		340				0.03	210	310	8.5			
IWTP 8	Metals Sludge solids	3400			42514	31				8.5		840	570
IWTP 8	Metals Sludge composite		28540							8.8	8.9		
IWTP 8	Metals Sludge composite PNNL		22300	150	25714	354				OC			53
IWTP 9	Aeration Basin Influent	390 ??	230	<---133			0.04	330	290	6.2	8.2		
IWTP 10	Biosludge - composite PNNL		3800	260	9943	15.33				8.47			
IWTP 10	Biosludge - composite	280	28540			0.02	0.028						
IWTP 10	Biosludge - solids - filtered	280	28540			0.10				7.6	8.3		
IWTP 11	Mixed Sludge Composite PNNL		153900	8000	288000	4020						21000	20000
IWTP 11	Mixed Sludge Solids ^(a)									7.3			
IWTP 11	Mixed Sludge composite (a)	24000	1168			679	1.2					Barium --- >	1.3
IWTP 11	Mixed Sludge TCLP extracted 6/95											Barium --- >	1.9
IWTP dry	Dried Sludge TCLP extracted 6/95												
IWTP 13	Final Effluent	8	91							7.3			

Note: All values in ppm unless indicated otherwise

Bold face figures are long term averages

TABLE B-1. RESULTS OF SLUDGE STREAM ANALYSIS AT OC-ALC (Continued).

Stream no.	Stream description	Iron	Aluminum	Hexavalent chromium	Chromium	Lead	Nickel	Cadmium	Copper	Zinc	Iron portion of metals	RCRA metal hydroxides	RCRA metal hydroxides as portion of solids	Total known inorganic (metals as hydroxides)
IWTP 1b	D1/D2 Effluent (D3 effluent)	4500 ---->	>	3.9	7.20	0	0.09	0.06	0.09	0.59		15	0.86%	16
IWTP 2	Lift #2 Influent			0.148	0.32	0	0.04	0	0	0		0.7		1
IWTP 2	Lift #2 Influent (tests for EPA filing)				1.63			0.14	0.03	0.04	0.20	4	0.58%	4
IWTP 4	D3 Sludge (paint stripping)				7	0	0.05	0.04	0.10	0.47		14	0.27%	15
IWTP 5	Oil Separator Sludge			0	330	26	193	42	175			1,313	3.86%	1,313
IWTP 5	Oil Separator Sludge TCLP extracted	Hg ---	0.001		0.8	0		0.09				1.7		9
IWTP 6	Oil Separator Effluent			0.246								-	0.00%	
IWTP 7	Equalization Basin Effluent			0.046	0.31	0	0.02	0	0	0		0.6	0.05%	521
IWTP 8	Metals Sludge solids													
IWTP 8	Metals Sludge composite	1800	222		66	3	18	4	8	7	85%	180	0.60%	7,500
IWTP 8	Metals Sludge composite PNNL	718			99	1	8	2			87%	213	1.97%	1,589
IWTP 9	Aeration Basin Influent	12	0-->	0.015	0.38	0	0	0.03	0.02	0.27		0.8	0.03%	777
IWTP 10	Biosludge - composite PNNL	34			1.18	0	0	0			96%	2.7	0.08%	69
IWTP 10	Biosludge - solids - filtered	6.8			0.05	0	0	0	0	0	99%	0.1	0.01%	13
IWTP 10	Biosludge - solids - filtered	6.2			0.22	0.00	0.04	0.01	0.03	0.08	94%	0.6		13
IWTP 11	Mixed Sludge Composite PNNL	8220			1055	11	96	21			87%	2,282	1.97%	18,036
IWTP 11	Mixed Sludge Solids (a)	60000	7200		1460	71	479	125	244	141	86%	329	0.03%	18,104
IWTP 11	Mixed Sludge composite (a) italics calc. values	4620	554		112	5	37	10	19	11				
IWTP 11	Mixed Sludge TCLP extracted 6/95				0.87	0		0.02						
IWTP dry	Dried Sludge TCLP extracted 6/95				0.21	0		0						
IWTP 13	Final Effluent			0.032	0.01	0.00	0.01	0.00	0.00	0.00		0.03	0.00%	0.04

Bold face figures are long term averages

Note: All values in ppm unless indicated otherwise

RCRA metals: Chromium, Lead, Nickel, Cadmium, Copper; as hydroxides

Total Inorganics: As hydroxides of Chromium, Lead, Nickel, Cadmium, Copper, Aluminum, Iron, Calcium (as carbonate), Silicon (as oxide), Chloride, Sulfate, Nitrate

TABLE B-1. RESULTS OF SLUDGE STREAM ANALYSIS AT OC-ALC (Continued).

Stream no.	Stream description	Fixed solids (Ash)	Total volatiles	TSS	Total Dissolved Solids	Total Residue (total solids)	Oils and grease	TOC	TOC filtrate	C	H Net from moisture test and H test	C to N ratio (mol)	H to C ratio (mol)	N	S	Phenol
IWTP 1b	D1/D2 Effluent (D3 effluent)	0	496	496	1204	1700	16	2200						1092, 2500-->		637
IWTP 2	Lift #2 Influent	0		51	850	901										0.895
IWTP 2	Lift #2 Influent (tests for EPA filing)	0				610	13	55.2								0.895
IWTP 4	D3 Sludge (paint stripping)	8000				5200	2400	2000								750
IWTP 5	Oil Separator Sludge	32000	18000	50000		34000	16000	34000								250
IWTP 5	Oil Separator Sludge TCLP extracted													Cresols --->		0
IWTP 6	Oil Separator Effluent	0	810			810	0	122						160-->		51
IWTP 7	Equalization Basin Effluent	1100	300			1400	14									21
IWTP 8	Metals Sludge solids	7600	12400 <-- or	152		20000	2600	24000								
IWTP 8	Metals Sludge composite					30000										
IWTP 8	Metals Sludge composite PNNL	4000	7500	11500	180	10800		1730	44	4,175	669	9.5	1.9	514		
IWTP 9	Aeration Basin Influent	1400	1000			2400		14.6								
IWTP 10	Biosludge - composite PNNL	400	2900	3300	200	3300		366	41	1,515	227	6.3	1.8	281	0.57--	0.125
IWTP 10	Biosludge - composite	0	1900			1900		111								0.04
IWTP 10	Biosludge - solids - filtered	58	1942			2000		255								0.12
IWTP 11	Mixed Sludge Composite PNNL	32000	84000	116000	1000	116,000		34600	2678	44,312	7,180	12	1.9	4,304		
IWTP 11	Mixed Sludge Solids (a)							62000								
IWTP 11	Mixed Sludge composite (a)	30000	47000	77000		61000				50,400	4,844		1.15	2,800		50
IWTP 11	Mixed Sludge TCLP extracted 6/95													Cresols --->		4.1
IWTP dry	Dried Sludge TCLP extracted 6/95													Cresols --->		1.6
IWTP 13	Final Effluent	0		10		880	2									0.010

(a) Entries for composite sludge: fixed, volatile, residue and suspended solids, as measured. Elemental analysis calculated from solids analysis.

Bold face figures are long term averages

Note: All values in ppm unless indicated otherwise

TABLE B-3. RESULTS OF STREAM ANALYSIS AT OO-ALC.

		Total Petroleum Hydrocarbon	48300	27700
APHA - 2540 B or G for semisolids		Total Residue (total solids)	11.0%	50.8%
200.7/289.1		Zinc	828	2753
200.7/220.2		Copper	1232	3933
200.7/213.2		Cadmium	632	1829
200.7/249.2		Nickel	3011	5310
200.7/218.2		Chromium	33049	102067
200.7/202.1		Aluminum	5538	18289
200.7/215.1		Calcium	22855	68241
200.7/236.2		Iron	7900	27532
EPA Method	Stream no.	Stream description	Sludge Thickener Underflow	
			Sludge from Dryer	
	IWTP 6			
	IWTP 7			

Note: All values in ppm unless indicated otherwise

APPENDIX C

LABORATORY PRESSURE FILTRATION APPARATUS AND PROCEDURE, SAMPLE FLOCCULATION AND PRESSURE FILTRATION DATA LOGS

APPENDIX C

LABORATORY PRESSURE FILTRATION APPARATUS AND PROCEDURE, SAMPLE FLOCCULATION AND PRESSURE FILTRATION DATA LOGS

A JWI three inch laboratory plate and frame filter press was leased from the manufacturer. A diagram of the bench filter press is provided in Figure C-1. The press is composed of four major assemblies: (a) the sludge reservoir that holds the sludge under pressure (23); (b) the pressure filtration chamber where filtration occurs and the filter cakes is deposited (12 and 13); (c) the hydraulic ram supplies the pressure to seal the plates in the press (14); (d) the clamp that holds the chamber parts together (1 through 10). The press is assembled on the clamp (serves as the filter press frame) with the filter cloths between the 3 inch (2 inches internal diameter) filter chamber (13) and the support plates (12) and the hydraulic ram head (21) is inserted between the swivel pad (10) at the end of the clamp screw (7). The hydraulic ram (14) provides a 6,000 psi pressure at its head (21) that is used to seal the filter chamber, the ram has a pressure gage (18) to monitor hydraulic pressure. Sludge is supplied from the sludge reservoir (23) through the supply tube (27) to the filter chamber (13) once the female connector (29) is hooked up to the male connector (30) on the filter chamber. The filtration pressure is supplied externally from a regulated high pressure nitrogen cylinder that is connected to the pressure regulator (24). The sludge reservoir is mounted on top of a vortexer (not shown) that vibrates the sludge reservoir and prevents clogging of the feed tube (27) when sludge particles dewater in the reservoir. The filtrate is collected at the nozzles (31,33) on the bottom of the support plates.

The procedure for a pressure filtration is as follows:

- (1) Place the end plates and the filter chamber on the press body with the filter chamber in the middle and the end plates oriented with their rectangular indented surface facing outwards.
- (2) Place filters in the gaps between the end plates and the filter body with the smoother side oriented towards the chamber. Make sure the filter protrudes symmetrically from all sides.

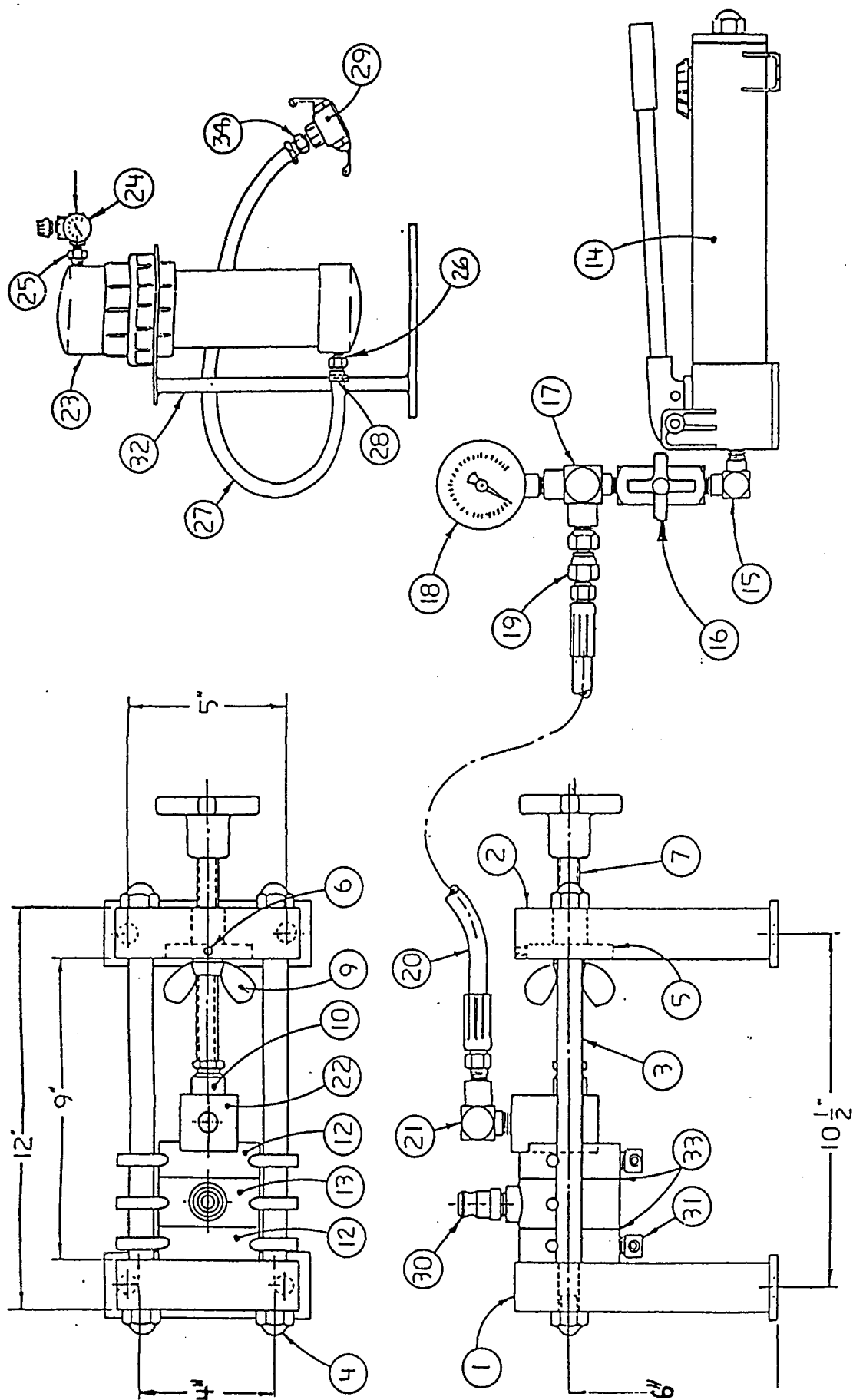


Figure C-1. Schematic of Apparatus for Pressure Filtration Tests.

- (3) Put in the hydraulic ram head with the concentric circle portion facing the end plate. Check positioning of the filter cloths and the filter components.
- (4) Tighten the clamp mechanism of the filter press with the large handle and then tighten the butterfly nut. Pump the hydraulic ram to 6000 psi. Attach the filtrate tubes and place the output in the collection vessel.
- (5) If precoat is needed, measure out 2 grams of the precoat material (Celite Hyflo Super Gel) and mix with one liter of water in a 1 liter beaker. Keep stirred till use.
- (6) Place the feed tank on its stand and in the vortexer. Attach the feed tube to the filter chamber connector. Fill the tank with the precoat solution (if needed) or the sludge. Close the top of the feed tank and tighten the flange and close the regulator.
- (7) If running a precoat, raise the pressure to 10 psi by setting the pressure regulator. Keep running till air comes through (there is bubbling in the bubbling in the collection vessel).
- (8) For sludges, raise the pressure to the required level and measure the volume of filtrate every 5 min. For the first pressure cycle measure the time for the first 10ml, 20ml, 30ml. Run till the end point criterion (filtration rate of 2 ml/min or less unless otherwise specified) is reached.
- (9) Repeat 8 for each of the pressures (25, 50, 75, 100 psi).
- (10) Pressure release at the end of precoating or the end of filtration: Close the regulator on the cylinder, Release the air through the feed tank regulator, Release excess air through the valve on the cylinder regulator. Open the flange and remove the cap from the feed tank.

- (11) Add the required additional sludge, if needed, and repeat 6-7.

Final release of sludge filter cake:

- (12) Remove the feed tank from the vortexer and the stand. Keeping the feed tank well below the level of the filter chamber, release the feed tube connector and carefully release the connector from the filter chamber. Pour out the remaining sludge. Weigh the total filtrate.
- (13) Release the hydraulic pressure by opening the valve by the tube connection. Unscrew the butterfly nut and the large screw. Remove the ram and carefully open the filter chamber. Note the condition of the cloth and remove the filter chamber from the press assembly with the filter cake.
- (14) Remove filter cake onto a weighed weighing tin and weigh it after careful removal of the filter cloths. Place to dry in the oven. After $\frac{1}{2}$ an hour in the dryer connect the vacuum pump and run it till the vacuum level stabilizes at 25 psig. Then release the vacuum and remove the sample for weighing at repeat least once, for a better than 2 percent match in weights.
- (15) Wash all the parts.

Date 04/22/96 Run: 2 ml criterion
Warner Robbins

Turbidity: 6.1

Test: 25 cfm cloth new filter no precoat

Filter Cake Wt. (gms): 72.21
Filter Cake in wt. (gms): 1.595
Net Filter Cake wt. (gms): 70.615
Total Slurry Collected: 737.7

Moisture Analysis	
Tare Wt. (gms):	1.595
Initial wt. (gms):	21.136
Final wt. (gms):	6.578
Solids content	
25.5%	

Time (min)	Press. (psig)	Total Filtrate Wt. (gms)	Flow Rate (ml/min)	Calculate	
				Solids content	Vol. Reduc.
0.00	0	12.9		4.6%	
5.00	25	53.3	8.08	7.4%	35%
10	25	73.4	4.02	8.9%	45%
15	25	88.6	3.04	10.0%	51%
20	25	100.9	2.46	10.8%	55%
25	25	111.2	2.06	11.6%	58%
30	25	120	1.76	12.2%	60%
35	50	132.2	2.44	13.1%	63%
40	50	141.1	1.78	13.7%	65%
45	50	149.5	1.68	14.3%	66%
50	75	159.8	2.06	15.0%	68%
55	75	168	1.64	15.6%	69%
60	75	175.5	1.50	16.2%	70%
65	100	184.2	1.74	16.8%	71%
70	100	191.7	1.50	17.3%	72%
75	100	198.5	1.36	17.8%	73%

Total filtrate + leaks: 205.4

TABLE C-1. PRESSURE FILTRATION OF WR-IWTP #2 SLUDGE WITHOUT FLOCCULANT, USING A 25 cfm CLOTH.

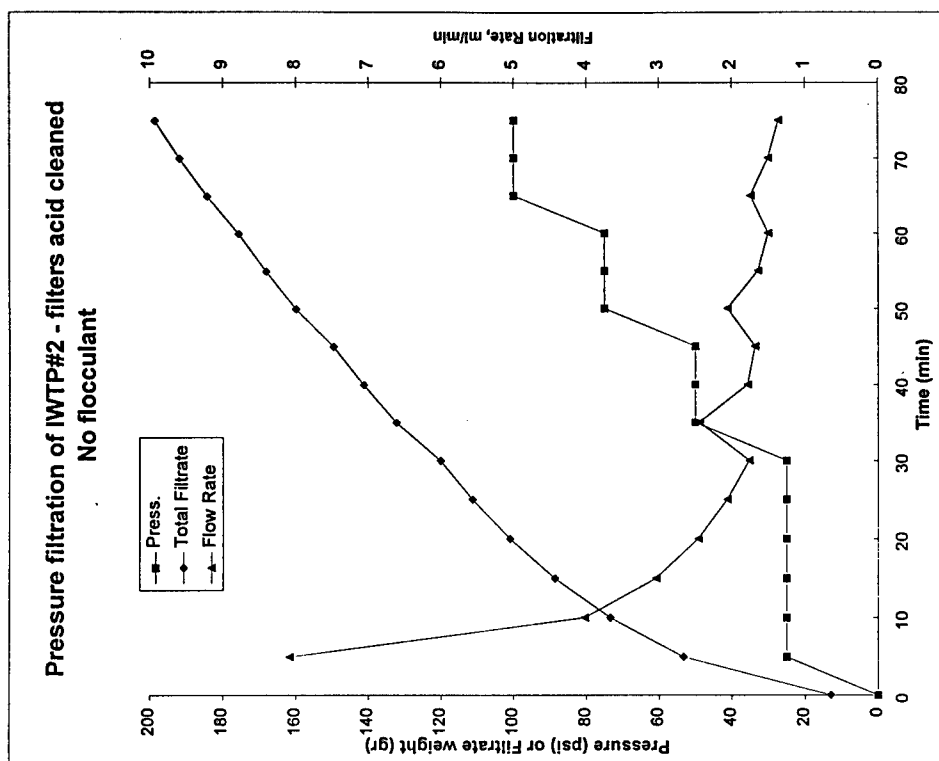


Figure C-2. Pressure Filtration of WR-IWTP #2 Sludge Without Flocculant, Using a 25 cfm Cloth.

Date 04/22/96 Run: 2 ml criterion
Warner Robbins

Test: 25 cfm cloth new filter no precoat

Flocculant	Concentration	dilution	Loading lb/	Actual loading
Cytec 1820	1000 ppm	none	18.4	18.4
			Actual addit	280
			Final sample weight(gms):	680.00
Sample Net wt. (gms):	500			

Net Filter Cake wt. (gms): 72.6

Total Slurry Collected: 241.6

Moisture Analysis	
Tare Wt. (gms):	1.019 pan
Initial wt. (gms):	11.753 with pan
Final wt. (gms):	4.16 with pan
Solids conte	29.3 %

Total In: 841.3

Total Out: 807.5

Time (min)	Press. (psig)	Total Filtrate Wt. (gms)	Flow Rate (ml/min)	Calculate Solids content	Vol. Reduc.
0.00	0	83.8		10.0%	50%
5	25	203.8	24.00	18.9%	73%
10	25	248.5	8.94	22.3%	77%
15	25	284.6	7.22	24.9%	80%
20	25	315.5	6.18	27.2%	81%
25	25	343.7	5.64	29.3%	83%
30	25	367.2	4.70	31.1%	84%
35	25	383.3	3.22	32.3%	84%
40	25	392.3	1.80	32.9%	85%
45	50	407.7	3.08	34.1%	85%
50	50	418.4	2.14	34.9%	86%
55	50	427.4	1.80	35.6%	86%
60	75	438.2	2.16	36.4%	86%
65	75	447.2	1.80	37.0%	86%
70	75	455.1	1.58	37.6%	87%
78	100	469.2	1.76	38.7%	87%
85	100	479.7	1.50	39.4%	87%

Total filtrate + leaks: 493.3

TABLE C-2. FLOCCULATION AND PRESSURE FILTRATION OF WR-IWTP #2 SLUDGE FLOCCULATED WITH CYTEC 1820 (LOADING OF 18.4 lb/ton DS).

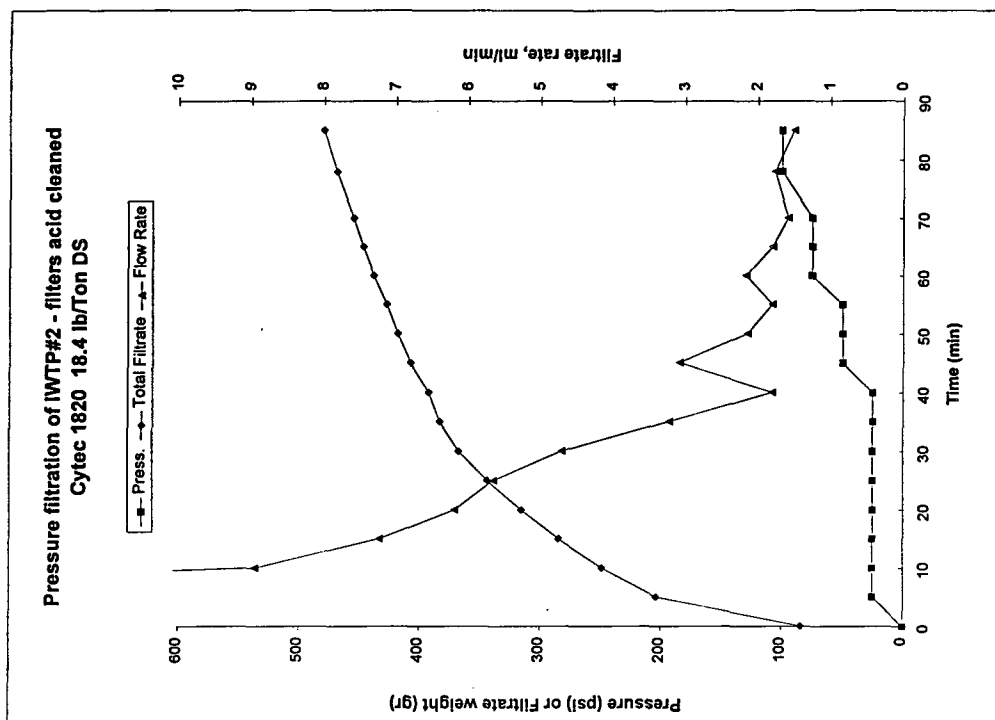


Figure C-3. Flocculation and Pressure Filtration of WR-IWTP #2 Sludge Flocculated with Cytec 1820 (loading of 18.4 lb/ton DS).

Date Run: 2 ml criterion Warner Robbins

Test: 25 cfm clot new filter no precoat

Floculant		Concentrati dilution		Loading lb/ Actual loading		Cumulative polymer ad Observations	
Percol 727	500 none	<4	3.6	Small flocs			
was a little old		ppm	Max additio Actual addi	Addition steps			
			60 ml	110			
Net wt. (gms):		500		Final sample weight(gms):		610.00	

Initial vol. (ml): 610
Initial wt. (gms): 1104.9
Beaker Tare wt. (gms): 383.9
Net Wt. (gms): 721
Resid. wt. (gms): 383.9
otal used in test (gms): 721

Net Filter Cake wt. (gms): 72.8

Total Slurry Collected: 259.3

Time (min)		Press. (psig)	Total Filtrat Wt. (gms)	Flow Rate (ml/min)	Vol. Reduc.	Calculate Solids content
0.25	25	30	16.22	6.3%	16%	
0.62	25	40	22.22	7.1%	25%	
1.07	25	50	17.65	7.9%	33%	
1.63	25	60	16.22	8.7%	39%	
2.25	25	70	13.33	9.5%	44%	
3	25	80	12.00	10.2%	48%	
3.8	25	90	12.86	11.0%	52%	
5	25	105	12.86	12.2%	56%	
13	25	158.7	6.71	16.4%	68%	
24	25	200.8	3.83	19.7%	73%	
31	25	222.6	3.11	21.4%	75%	
33	25	228.6	3.00	21.9%	76%	
37	25	238.8	2.55	22.7%	77%	
45	25	254.5	1.96	23.9%	78%	
51	50	271.7	2.87	25.2%	79%	
58	50	286.8	2.16	26.4%	80%	
62	50	297.8	2.75	27.3%	81%	
68	75	313.3	2.58	28.5%	81%	
70	75	318.1	2.40	28.9%	82%	
77	75	331.5	1.91	29.9%	82%	
82	100	343.1	2.32	30.8%	83%	
91	100	360.2	1.90	32.2%	83%	
99	100	371.6	1.43	33.1%	84%	

Moisture Analysis	
Tare Wt. (gms):	1.013
Initial wt. (gms):	15.067
Final wt. (gms):	5.106
Solids cont	29.1%

Total In: 721
Total Out: 708.2

Total filtrate + leaks: 376.1

TABLE C-3. FLOCCULATION AND PRESSURE FILTRATION OF WR-IWTP #2 SLUDGE FLOCCULATED WITH PERCOL 727 (LOADING OF 3.6 lb/ton DS).

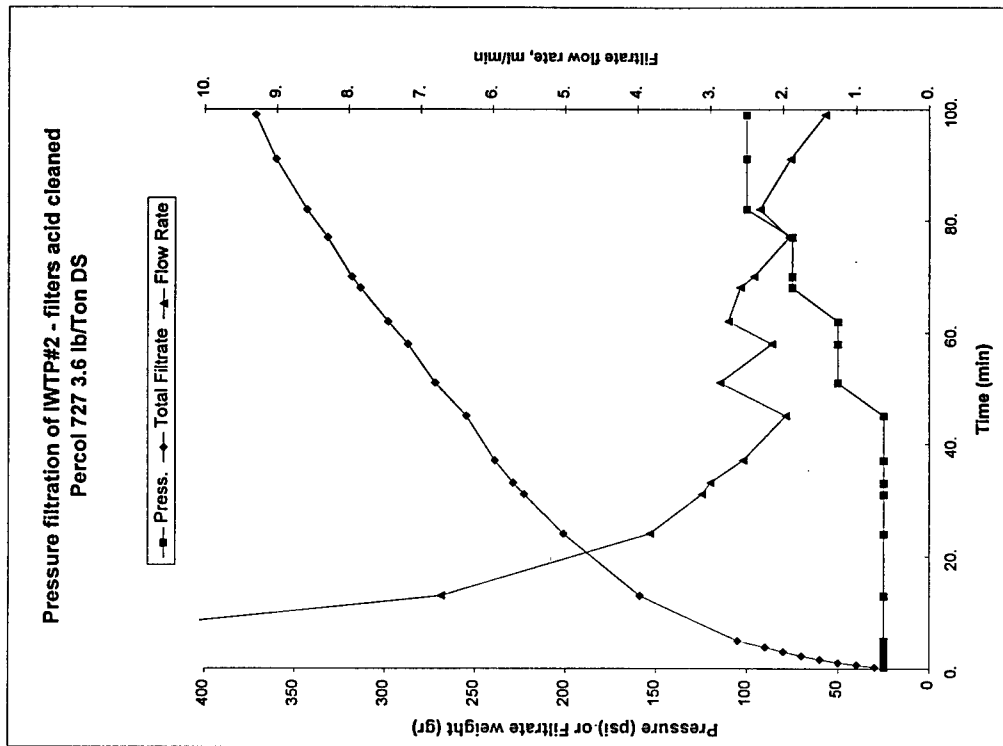


Figure C-4. Flocculation and Pressure Filtration of WR-IWTP #2 Sludge Flocculated with Percol 727 (loading of 3.6 lb/ton DS).

APPENDIX D

**RESULTS OF FLOCCULATION AND PRESSURE
FILTRATION EXPERIMENTS**

APPENDIX D

RESULTS OF FLOCCULATION AND PRESSURE FILTRATION EXPERIMENTS

The detailed results of the flocculation and pressure filtration experiments discussed in Section V.B are given in the tables below. The raw data of flocculation and pressure filtration experiments were not included because of the great number of data entries, samples of the data logs for typical filtration experiments were provided in Appendix C.

Table D-1 contains the flocculation data for the polymer screening of WR-IWTP #17 and is discussed in Section IV.B.4. The pressure filtration data are tabulated in Table D-2. Table D-3 contains the flocculation data for the polymer screening of WR-IWTP #2 and is discussed in Section IV.B.5. The pressure filtration data are tabulated in Table D-4.

Table D-5 contains the flocculation data for the polymer screening of OC-IWTP #11 and is discussed in Section IV.B.6.

**TABLE D-1. RESULTS OF POLYMER SCREENING FOR WR-ALC
SLUDGE IWTP#17.**

Sample Date	Polymer	Polymer Loading (lb/ton_{DS})	Comments	Effect	Solids content in filter cake
1/25/96	Calgon, Pol-E-Z-6400	14.7	Maximum loading	No effect	
1/25/96	Calgon, Pol-E-Z-675	14.7	Maximum loading	No effect	
1/25/96	Calgon, Pol-E-Z-692	14.7	Maximum loading	No effect	
1/17/96	Cytec 1598C	7.8	Maximum loading	No effect	
1/25/96	Cytec 1820A	13.7	Maximum loading	No effect	
1/25/96	Cytec 1839A	13.7	Maximum loading	No effect	
1/25/96	Cytec 1883A	13.7	Maximum loading	No effect	
1/17/96	Cytec 1885A	7.8	Maximum loading	No effect	
1/17/96	Cytec 1906N	7.8	Maximum loading	No effect	
1/25/96	Cytec 836A	5.9	Large Flocs	Flocculated	10.7%
1/25/96	Cytec 837A	5.9	Very Large Flocs	Flocculated	10.9%
1/25/96	Cytec 866A	7.8	Large Flocs	Flocculated	10.1%
1/17/96	Nalco 7194	15.7	Maximum loading	Not sure	11.8%
1/17/96	Nalco 7768	15.7		Flocculated	12.9%
4/8/96	Nalco 7768	11.6		Flocculated	10.6%
4/8/96	Nalco 7768	13.7		Flocculated	
4/8/96	Nalco 7768	12.5		Flocculated	
1/25/96	Percol 725	2.5	Large Flocs	Flocculated	12.7%
1/25/96	Percol 726	2.9	Maximum loading	No effect	
1/25/96	Percol 727	2.9	Small Flocs	Flocculated	13.4%
4/8/96	Percol 727	2.7		Flocculated	
4/8/96	Percol 727	3.1		Flocculated	

**TABLE D-2. RESULTS OF PRESSURE FILTRATIONS FOR WR-ALC
SLUDGE IWTP #17 WITH DIFFERENT POLYMERS.**

Sample date	Polymer	Loading (lb/Ton _{DS})	Criterion (ml/min)	Filtration time (min)	Turbidity (NTU)	Solids content	Specific resistance (X10 ⁷ sec ² /g) at 25 psi
Jan-96	Nalco 7168(E)	9.0	2		13	24%	
Apr-96	Nalco 7168(E)	11.6	2	75	104	22.7%	235
Apr-96	Nalco 7168(E)	12.5	2	75	35	23.1%	201
Jan-96	Nalco 7168(E)	13.5	2		25	24%	
Apr-96	Nalco 7168(E)	13.7					
Apr-96	Nalco 7168(E)	13.9	1	175		26.3%	293
Apr-96	Nalco 7168(E)	14.8	1.5	85		23.5%	180
Jan-96	Nalco 7168(E)	18.0	2		28	20%	
Apr-96	Percol 727(P)	2.4	2	86		25.9%	133
Jan-96	Percol 727(P)	2.5	2		64	23%	
Apr-96	Percol 727(P)	2.7	2	70	34	21.6%	128
Apr-96	Percol 727(P)	3.1	2	65		21.4%	159
Apr-96	Percol 727(P)	3.3	1.5	135	27	26.8%	153
Apr-96	Percol 727(P)	3.8	1.5	175		28.7%	143
Apr-96	Percol 727(P)	3.8	1	175	3.5	29.2%	148
Apr-96	Percol 727(P)	4.3	1.5	140		28.1%	184
Jan-96	No treatment		1	240		27.1%	

**TABLE D-3. RESULTS OF POLYMER SCREENING FOR
WR-ALC SLUDGE IWTP#2.**

Sample Date	Polymer	Polymer Loading (lb/ton _{DS})	Effect	Solids content in filter cake	Filtrate Turbidity (NTU)
4/29/96	Calgon, Pol-E-Z-692	6.0	Flocculated	15.6%	0.8
4/29/96	Calgon, Pol-E-Z-692	7.5	Flocculated	14.2%	1.2
4/29/96	Calgon, Pol-E-Z-692	9.0	Flocculated	14.6%	0.95
4/29/96	Cytec 1820A	13.7	Flocculated	13.5%	0.9
4/29/96	Cytec 1820A	14.9	Flocculated	11.5%	4.1
4/29/96	Cytec 1820A	18.7	Flocculated	13.4%	4.1
4/29/96	Cytec 836A	1.9	Flocculated	16.0%	1.6
4/29/96	Cytec 836A	2.4	Flocculated	15.9%	1.4
4/29/96	Cytec 836A	3.0	Flocculated	14.4%	0.8
4/29/96	Percol 727	1.5	Flocculated	16.7%	1.2
4/29/96	Percol 727	1.9	Flocculated	15.0%	1.1
4/29/96	Percol 727	2.4	Flocculated	15.8%	1.3

**TABLE D-4. RESULTS OF PRESSURE FILTRATIONS FOR WR-ALC
SLUDGE IWTP#2 WITH DIFFERENT POLYMERS.**

Polymer	Loading (lb/Ton _{DS})	Filtration time (min)*	Number of filter cloth reuses	Solids content	Specific resistance (X10 ⁷ sec ² /g) at 25 psi
Calgon, Pol-E-Z-692	8.8	80		26.1%	204
Cytec 1820A	18.4	85		29.3%	108
Cytec 1820A	16	80		25.9%	190
Cytec 1820A	14.0	80	4	28.3%	159
Cytec 1820A	15.4	80	3	28.9%	158
Cytec 1820A	13.8	80	2	28.9%	158
Cytec 1820A	11.9	80	1	29.0%	203
Cytec 837	3.5	90		25.9%	124
Percol 727	3.6	99		29.1%	81
No treatment		75		25.5%	180

**TABLE D-5. RESULTS OF ANIONIC POLYMER SCREENING
FOR OC-ALC SLUDGE IWTP #11.**

Sample Date	Polymer	Polymer Loading (lb/ton _{DS})	Effect	Filtration Time (min)	Solids content in filter cake	Filtrate Turbidity (NTU)
4/8/96	Calgon Pol E Z 675	8.5	No effect			
4/8/96	Calgon Pol E Z 692	20	Slight flocculation	Did not	filter	
4/8/96	Calgon Pol E Z 692	25	Slight flocculation	Did not	filter	
4/8/96	Calgon Pol E Z 692	30	Slight flocculation	Did not	filter	
4/8/96	Cytec 1820A	20.0	Slight flocculation	15	8.1 %	
4/8/96	Cytec 1820A	25.0	Slight flocculation	15	7.9 %	
4/8/96	Cytec 1820A	30.0	Slight flocculation	15	8.1 %	
4/8/96	Cytec 1820A	45.1	Flocculated	15	9.7 %	384
4/8/96	Cytec 1820A	13.5	Some coagulation	15	6.7 %	400
4/8/96	Cytec 1820A	9	No effect			
4/8/96	Cytec 1883A	9	No effect			
4/8/96	Cytec 835A	1.8	Slight flocculation	15	9.5 %	480
4/8/96	Cytec 835A	2.5	Slight flocculation	Did not	filter	
4/8/96	Cytec 836A	3.2	Flocculated	30	12.0 %	
4/8/96	Cytec 836A	3.5	Flocculated	30	12.8 %	
4/8/96	Cytec 836A	2.3	Flocculated	15	6.9 %	476
4/8/96	Cytec 836A	2.5	Flocculated	15	8.9 %	366
4/8/96	Cytec 836A	1.4	Slight flocculation	15	7.8 %	472
4/8/96	Cytec 836A	1.6	Slight flocculation	15	12.5 %	552
4/8/96	Cytec 837A	1.6	Some flocculation			

**TABLE D-5. RESULTS OF ANIONIC POLYMER SCREENING
FOR OC-ALC SLUDGE IWTP#11 (CONTINUED).**

Sample Date	Polymer	Polymer Loading (lb/ton _{DS})	Effect	Filtration Time (min)	Solids content in filter cake	Filtrate Turbidity (NTU)
4/8/96	Nalco 7768	22.6	Flocculated	30	8.9 %	
1/24/96	Nalco 7768	13.6	Slight coagulation			
4/8/96	Percol 725	1.9	Flocculated (small)	15	9.9 %	384
4/8/96	Percol 725	3.6	Some flocculation	30	13.6 %	
4/8/96	Percol 725	4.0	Some flocculation	30	13.0 %	
4/8/96	Percol 725	1.4	Some flocculation	15	9.6 %	416
4/8/96	Percol 725	4.5	Flocculated	30	8.4 %	
4/8/96	Percol 725	2.0	Some flocculation	30	8.4 %	
4/8/96	Percol 725	2.7	Some flocculation	30	8.8 %	
4/8/96	Percol 725	3.4	Some flocculation	30	8.6 %	
4/8/96	Percol 727	2.7	No effect			
4/8/96	Percol 727	2.1	No effect			
4/8/96	Percol 727	4.5	Some particulation	Did not	filter	
1/24/96	Percol 727	3.3	Initial Flocculation	30	8.4%	

APPENDIX E

SURVEY OF SELECTED THERMAL DRYING SYSTEMS

APPENDIX E

SURVEY OF SELECTED THERMAL DRYING SYSTEMS

A number of vendors were contacted to determine the feasibility of various processes for drying the metal hydroxide sludges. A description of four of these drying systems is provided below.

A. FLASH DRYING

Flash dryers utilize a tube design in which material is "thrown" into the hot air stream. The design allows for good mixing of the feed and the hot air and, therefore, requires only a short residence time (on the order of seconds to minutes). The flash dryer is basically a glorified duct with heating: material is simultaneously evaporated and conveyed. A relatively high surface area created provide a high heat and mass transfer rates. Flash dryers are best utilized with materials that have primarily surface-related moisture, as opposed to moisture that is bound in the interior of the solid particles. Flash dryers would not be as effective for materials with interior-bound moisture, which would require a longer residence time.

Based on an initial sample evaluation, NIRO found that mechanical dewatering may make the sludge suitable for flash drying. An evaluation of filter cake sample would be necessary to determine the feasibility of flash drying. Flash drying without mechanical dewatering as a preliminary step would require enormous amounts of energy as well as large fans to drive through the necessary high volumes of air. A flash drying unit for a mechanically dewatered sample would only require conveying the sludge, not atomizing it (as in spray drying). Basically, the flash drying vessel would consist of duct work with a heater.

A variation of the flash dryer, called a ring dryer, may be well suited to sludge drying applications. In this adaptation, an extra manifold is used to recycle a portion of the feed stream, mixing it with dried product in a backmixing process. While this increases the overall residence time, the drying effectiveness is increased.

1. **Advantages.** Flash drying's short residence time makes it an effective drying technology for materials with externally-bound (surface) water. It is simplistic in design and includes no moving parts that require replacement.

2. **Disadvantages.** Flash drying is not as effective at removing internally bound moisture. However, the ring dryer, with its longer residence time, may overcome this problem.

3. **Applicability.** Flash drying may be a viable option, particularly after mechanical dewatering (filter press).

B. SPRAY DRYING

The spray drying process involves atomization of a liquid stream and intimate mixing with a heated gas within a drying chamber to effect the desired heat and mass transfer. The water is vaporized and the gas is cooled, producing spherical solid particles. Common industrial applications for spray drying are in the food and chemical industries, where the range of powder particle sizes produced is critical. In the case of sludge dewatering, the primary objective is simply to dry the sludge and remove unwanted moisture, and the size and quality of the particles produced is unimportant.

Spray drying incorporates the following elements: a method for atomizing the solution; a source of heat or hot air; a mixing chamber with adequate residence time and droplet/particle trajectory; a solids recovery system; and a fan for induction. Atomization is achieved in one of three ways: pressure (hydraulic) nozzles; two-fluid nozzles; and centrifugal (rotary) means. Pressure nozzles force fluid through an orifice; these nozzles are probably not ideal for the sludge drying application because the nozzles would tend to clog. Two-fluid nozzles mix the liquid feed with a compressed gas (usually air), which provides the atomization energy. Clogging would be less of an issue for this type of nozzle, but abrasion and corrosion of the nozzle itself (from the atomization of metal compounds/particulates) would be potential concerns. Two-fluid nozzles also require compressors and have the highest energy requirements of the three atomization systems. Centrifugal or rotary atomization involves feeding the liquid through an annular opening

to the center of a rotating wheel, spreading the fluid into a thin film. This method would perhaps be the most suitable for drying sludge because it would minimize complications of clogging and abrasion.

1. **Advantages.** Spray drying incorporates evaporative cooling, which permits drying without thermal degradation. In addition, atomization creates large surface areas for evaporation, enabling a short residence time. Furthermore, since the liquid feed contacts only a small portion of the drying system, corrosive elements do not affect much of the drying chamber and, therefore, common materials, such as carbon steel, can be processed as the primary material of construction.

2. **Disadvantages.** The feasibility of atomizing the sludge at all may be problematic because of its rubbery viscous character. Furthermore, the overall cost of the system may be high. Nozzle systems would have additional expenses, including auxiliary equipment such as air compressors, and frequent nozzle replacement. Operation and maintenance of the nozzle systems would also be problematic because of clogging and corrosion.

3. **Applicability.** At an incoming solids level of 6.5 to 10 percent solids, NIRO found that the sludge could easily be spray dried. The spray dryer would be a rotary, single point spray dryer with a bag house filter. A 1/4" orifice should be sufficient to avoid clogging.

C. **PULSE DRYING**

Pulse drying is achieved when a high moisture content material is introduced into the exhaust stream of a specially designed burner which is a valveless pulse combustor. The sonic shock created by the operation of the pulse combustor, operating at about 250 cycles per second, separates the feedstock into many fine droplets and particles. Thus, the surface area of the particulate exposed to the hot exhaust gases is greatly increased, facilitating efficient evaporation. The process is continuous; the actual drying requires only about 5 milliseconds, and the entire cycle from product injection to recovery lasts about one minute. Although operating temperatures in the pulse combustor exceed 2,500 F, because of the short residence/contact time,

the solids never reach a temperature higher than 100 to 125 F. System temperatures are maintained at around 175 to 225 F. Because these temperatures are lower than for conventional dryers, odor problems do not normally occur. Offgas temperatures are typically 165 F.

In a pulse jet dryer air is introduced into the system through an air column and is drawn into the combustor room and around the pulse combustor. The room can accommodate either one or more pulse combustors. Wet material enters the system through a feed pipe, and is injected into the drying cone of the combustor. Dry product and water vapors are blown from the drying cone into the primary collector, where the heavier dry particles are separated by gravity. Vapors and fine particles continue through the system to the dust collector, where the fine particles are removed by centrifugal action in the gas stream. Dry product falls out of the system through airlock valves and into a dry material conveyor, while vapors are drawn out of the system by a fan. The exiting water vapors pass through air quality control devices before being vented to the atmosphere.

The pulse combustor is always operated at its full power setting, creating a constant energy input to the system. Regardless of the raw material feed rate, the system removes a nearly constant amount of water per hour from the feedstock, approximately 2,700 lbs/hr. The amount of water removed from a raw material is controlled by varying the raw material feed rate.

Raw materials ranging from 1 to 99 percent moisture can be dried using the pulse drying system. Materials that have been successfully dried include sewage sludge and industrial plating waste. The removal of water from extremely oily materials has required the introduction of pre- and post-treatment processing to compensate for the effects of combustion emissions. However, oily products have been successfully dried.

System Size: The basic pulse drying system requires a space of 35 feet by 15 feet by 18 feet high. This space houses one (or two) pulse dryers to handle 25 (or 50) wet tons per day of raw product. The system includes a combustor room, primary collector, dust collector (multi-cyclone or baghouse), inlet and exhaust fans, air ducting, motor controls, and console. The system can be installed with existing belt presses, vacuum filters, or centrifuges.

D. FLUID BED DRYING

In a fluidized bed system, the reactor is continuously charged with a feedstream which is fluidized by a suitable inert gas, such as hot air. The reactor may also be heated to maintain the appropriate temperature for drying.

In the first zone of the fluid bed, there is a constant rate drying period in which free surface water is evaporated and the bed temperature equilibrates at the inlet air's adiabatic saturation temperature. Once all the surface moisture is removed, the bed temperature rises and approaches the fluidizing air temperature. The offgases may be outlet to a scrubber or an afterburner depending on the application. The fluidizing gases may be preheated before entering the drying vessel, using electricity or natural gas as a heat source.

Continuous fluid bed dryers have been used to dry suspension grade polymers including PVC, polypropylene, and polyethylene, in indirectly heated plug flow dryers. Sludges have also been treated in fluid bed dryers.

For dewatering sludges, a possible design would include an initial, "starter" fluidized bed of particles such as sand or alumina. The liquid sludge would be fed into the bed so that it coats the particles. The moisture from this surface layer would evaporate, and gradually the fluidizing particles would grow in size as the solid content of the sludge is deposited over time onto the existing particles. The solid particles would be continuously removed.

1. **Advantages.** Fluid bed dryers provide high heat transfer rates and intimate gas/solids contacting. Therefore, they have low operating temperatures and reduced residence times. In contrast to spray drying, high pressure is not involved, and corrosion and abrasion are not problems. The most economical, practical way to utilize fluid bed dryers may be to first remove moisture down to about 50 percent, and then utilize the fluid bed dryer to achieve 15 percent moisture or less.

2. **Disadvantages.** Fluid bed dryers require a fluidizable material. Inorganic sludge at 90 percent water may act as a pumpable liquid, not a fluidizable solid. Furthermore, the sludge may not behave as a fluidizable material even at 90 percent water, and especially when reduced to

50 percent or less water; it could be a gooey mass that is difficult to handle. These handling difficulties are complicated by the fact that the compounds added at the IWTP, such as $\text{Fe}(\text{OH})_2$, are often difficult to dewater because water becomes trapped internally rather than on the surface.

3. **Applicability.** The sludge was found to be not suitable for fluid bed drying because of the small particle size. The fluid bed velocity would have to be very low in order not to entrain all the solids, and this low flowrate would consequently not have sufficient energy to dry the sludge.

E. CONTROL TECHNOLOGIES REQUIRED

All of the above technologies for dewatering sludges will likely require some sort of emissions control for particulates (PM-10) and possibly also for VOCs. Each drying system will likely produce different emission characteristics, depending on the exhaust air flowrate, system temperature, and entrainment. Based on the compositions of the sludges (primarily streams OC-ALC IWTP #11 and #5), a conservative estimate of the VOC emission rate is 28 lb/hr (based on 4 tons/day wet sludge throughput, assuming a continuous operation) or 122 tons/yr. Uncontrolled dust emissions are similarly difficult to predict. Based on a mass balance and assuming a very conservative entrainment rate of 50 percent, about 16 lb/hr particulates (uncontrolled) are estimated to be emitted (based on 4 tons/day wet sludge throughput). (If 3,000 cfm is assumed as the exhaust flowrate, this corresponds to about 8.9×10^{-5} lb/ft³.)

Georgia State Air Laws limit particulate emissions based on process throughput. Based on a throughput of 4 tons/day (assuming continuous steady state 24 hr/day operation), the emission limit would be 1.23 lb/hr particulates. If the 16 lb/hr particulate emission rate (uncontrolled) is accurate, 92 percent control would be required. [391-3-1-02 (2) (tt)] VOC emissions may not exceed 25 tons.

Particulate controls may include cyclones (or multi-cyclones), wet scrubbers, baghouses (fabric filters), or electrostatic precipitators (ESPs). VOC controls may include thermal or catalytic incineration, regenerative thermal oxidation, carbon adsorption, or wet scrubbing.

Cyclones or multi-cyclones may not be the most appropriate control technology because they are not as efficient at removing smaller particles ($< 10 \text{ mm}$) as larger particles. Since analyses of the ALC IWTP sludge streams suggests that smaller particles are predominant, cyclones may not effectively remove a significant portion of the particulate matter emitted.

Baghouse fabric filters are quite efficient at removing small particulates (PM-10). There are several possible configurations; one of the most promising for this application is a fabric filter baghouse with pulse jet cleaning.

Wet scrubbers may also effectively remove both fine particulates and VOCs. Wet scrubbers do generate an additional waste stream, however.

Catalytic incinerators for removal of VOCs may not be a viable option because the sulfur, chlorine, and heavy metal content (especially lead) in the gas may be sufficient to poison the catalyst.

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APPENDIX F

**LABORATORY TESTING PROCEDURES FOR
METAL SEPARATION TECHNOLOGIES**

APPENDIX F

LABORATORY TESTING PROCEDURES FOR METAL SEPARATION TECHNOLOGIES

Extractant Phase Preparation

As described above (Section VI.D.1.a.), the extractant needs to extract anionic chromium species. Such extractants are Alamine® 336 (trioctyl amine) and Aliquat® 336 (methyl trioctyl ammonium chloride). Twenty percent active was used. For the screening studies. (Note that the extractant concentration is set by thermodynamic equilibria and not by reaction stoichiometry). Due to the very dilute Cr levels present in the influent, future optimization work should also test the reduction of extractant use levels to about 2-5 percent. This optimization work was not a part of this screening study.

The extractant phase is prepared by combining, on a weight basis, 5.0 percent Exxal® 10, 20.0 percent Aliquat® 336 (or Alamine® 336), and 75.0 percent Aromatic® 150 solvent. The three liquids were blended for ca. 5 minutes. There is no significant exotherm, heat of mixing or dissolution of solids involved. Exactly 1000 g of each extractant phase was prepared.

Extractant pre-equilibration

This operation loads the exchangeable anion onto the extractant and cleans fresh extractant. It only needs to be performed on fresh extractant phase.

1. To a four liter beaker fitted with an overhead stirrer, thermometer, and standing in a tub of cold tap water, add 1.0 liter of DI water.
2. Start the mixer at medium speed (no spattering).
3. Slowly stir in 1.0 liter of concentrated hydrochloric acid. Allow the solution to cool to less than 40 C. (Not that non-corrosive acids could be used in this step, e.g., H_2SO_4 , for in-plant considerations).
4. Stir in the one liter of the Alamine® 336 extractant phase prepared above. Increase stirring, if needed, to insure complete blending of the two phases.
5. Blend phases for five minutes.
6. Transfer the emulsion to a large separatory funnel and let the phases break.
7. Drain and discard the bottom phase of excess hydrochloric acid.

8. Wash the top (extractant) phase by adding about an equal volume of DI water to the separatory funnel, shaking vigorously 60 seconds, then allowing the phases to separate (CAUTION - Always test and relieve pressure buildup when shaking separatory funnels).
9. Discard bottom aqueous phase (slightly acidic water).
10. The above wash procedure (steps 8 and 9 are repeated two more times).
11. The pre-equilibrated, washed extractant solution was transferred to a 1L storage bottle and labelled.

The above pre-equilibration and wash procedure was repeated to prepare a pre-equilibrated or washed Aliquat® 336 extractant solution.

Chromium(VI) Extraction Procedure

Each of the extractant solutions prepared above were tested for Cr^{VI} extraction from synthetic Cr^{VI} rinse water and matrix matched feed solution using the following procedure. This procedure was repeated for each sample listed in Tables VI.D.2 and VI.D.3.

- Step 1. In a clean 50 ml beaker suitable size to hold the total liquid volume under stirring conditions (see Tables 1 and 2 for total volumes expected), was placed one disc shaped magnetic stirrer, and then the two liquid phases.
- Step 2. A watch glass cover is added and then the beaker is placed on a magnetic stirrer at room temperature.
- Step 3. The phases are blended thoroughly but not excessively (i.e. both phases completely blended into an emulsion but without excessive spattering, vortex flow out, risk of stirrer stoppage).
- Step 4. The phases are blended 5.0 minutes.

Step 5. After the stirring period of Step 4, the emulsion is poured into a suitably sized graduate cylinder and the time (to the nearest 20 seconds) to ~50 percent and to ~90 percent volume separation recorded in the appropriate Table cell.

Step 6. If it is possible to obtain a good sample of the aqueous phase at this time, then this is accomplished by removing a suitable portion (ca. 4 cc) from the bottom phase by the following procedure:

- A disposable Pasteur pipette (a micro-pipette is better if available, this removes the need for a second pipetting later) is fitted with rubber bulb and inserted into the bottom being very careful to steadily blow out air while the tip is passing through the top phase (you might want to practice this procedure before the actual experiment since the pipette tip needs to be discarded if the top phase is inadvertently withdrawn into it).
- The bottom phase is then withdrawn into the pipette until no bulb vacuum remains.
- With a KimWipe® around the pipette, it is drawn from the beaker such that the top phase is wiped from the pipette outer surface.
- Finally the tip is blotted slightly to insure no top phase has been pulled into it.
- The sample within the pipette is then expelled into a sample vial .
- The sample is then analyzed for Cr^{VI} by either the Hach method, or for total Cr by the ICAP (or AA) method.

Step 7. If the emulsion in the graduate cylinder did not separate well, then, after taking the volume and phase separation time readings, the emulsion is transferred to a 50 cc plastic (PP) centrifuge tube and centrifuged. Then proceed with sampling of the bottom phase as per Step 6.

c. Preparation of SCC Blanket (Active Metal Hydroxide Absorbent) (47528-23)

Step 1. Calibrated the pH controller at 7.00 then at 10.00. Left the pH electrode in pH 10 buffer until needed. Adjusted the set point for the pH controller to 9.1.

Step 2. Prepared one liter of a 6 percent nitric acid solution by diluting 64 ml of concentrated nitric acid to 1.0 L with DI water with graduate cylinders. A magnetic stir bar was used in the 1L graduate cylinder to thoroughly mix the solution. Transferred this solution to a clean/new 1L polyethylene (Nalgene®) bottle and labeled "Stock 6 percent HNO₃ for dilute metal sample stabilization. Reference No. Exactly 1.000 ml of this solution is used for each 6.00 ml of sample solution (see below) to prevent metal precipitation between the time of sampling and the time of analysis. The feed solutions were treated with this solution in the same manner as the samples so that the ICP data are directly comparable.

Step 3. The amounts of each salt (except Pb to avoid premature precipitation of PbSO₄) given in Table 40 were added to a 1L volumetric flask containing ~800 ml DI water with stir bar and allowed to dissolve completely and mix thoroughly. The solution was then diluted to the mark and mixed thoroughly. The entire amount of solution was transferred to the clean beaker of the experimental apparatus (Figure 27). The lead acetate was then blended in imparting a milky white color of PbSO₄ precipitate.

- Step 4. The pH of the solution from (3) was measured at about 5 using the calibrated electrode.
- Step 5. Sampled 6.00 ml of the solution into a 10 cc labelled, polystyrene vial containing 1.000 ml of 6 percent HNO_3 . The vial was capped and mixed.
- Step 6. Insert the pH electrode and 1.000 N NaOH delivery tube were inserted into the solution from (4). The NaOH liquid level, tare weight and gross weight on the NaOH graduate cylinder reservoir was recorded.
- Step 7. With stirring at 300 rpm, the controller was turned on and the pH allowed to climb to 8.9. The main buffer regions were found to be around H 5.6 and 6.2 (consistent with $\text{Cu}^{\text{II}}/\text{Cr}^{\text{III}}$ and then Cd hydroxide precipitation, respectively). The pH adjustment took 33 min and consumed 35.0 ml of 1.000 N NaOH. The pH maintained in the 8.88-8.95 range for 50 minutes.
- Step 8. The stirring was slowed down to 30 rpm to allow the ½ in. thick blue green metal hydroxide blanket to form.

d. Preparation of Synthetic IWTP Influent Concentrate

- Step 9. To a one liter hot MICRO® cleaned beaker flask added ~ 800 ml DI water and stir bar.
- Step 10. To (9) added the three metal salts in the amounts given in Table 40. Stirred until completely dissolved. Then pH adjusted with mixing to 2.30 (target 2-2.5) using 6 percent nitric acid. After four days the pH was 2.35.
- Step 11. Quantitatively transferred (using dripless stir rod technique) the solution from (10) to a MICRO® cleaned one liter volumetric flask. Diluted to mark with DI water and mixed. Transfer this solution to a new/MICRO® clean 1L plastic (Nalgen or polyethylene) storage bottle and labelled as "Synthetic IWTP Metal Ion Feed Solution Concentrate".

e. Solids Contact Clarifier (SCC) Test (47528-24)

- Step 12. Increased the stirring in the solution from (8) just sufficient to resuspend the solids to the top of the liquid. RPM needed to do this was 120 rpm.
- Step 13. Reintroduced calibrated (pH 7.00, 10.00) pH meter, weight, and 0.1 N NaOH delivery tube with controller OFF. Record pH = 8.8.
- Step 14. Start controller with pH 8.9 setpoint. pH overshoot to 9.2, then leveled out at 8.96
- Step 15. Stirred 20 min. after the set point pH (8.9 ± 0.15) was reached. Then stop stirring and let solids settle. Very fluffy solids settled quickly to 200 ml blanket. Supernate was very clear and colorless with a small amount of particulates still present in the supernatant.
- Step 16. Using a 10 cc syringe, sample 7 cc of top 1 in. of liquid being very careful not to take any of the solid particulates. Filter this sample through a 0.2 μ Acrodisc® syringe filter pipe 6.00 ml of this sample into a sample vial with 1.000 ml 5 percent HNO_3 , capped and mixed.. Label.
- Step 17. Resuspended the solids by stirring to the same degree as was done in step (12).
- Step 18. Filled a 2000 μ l buret with 1000 ppm Pb AA standard, and a 25.00 ml buret with the synthetic IWTP feed (Step 11).
- Step 19. Added solutions from Step 18 and Step 11 dropwise over 30 minutes to the automatically pH controlled suspended blanket from Step 17. The pH tended to drop only very slowly and then enabled the pH controller to easily maintain the pH. Manual pH control was equally effective. Final pH was 8.86 with the range during the experiment being 8.8-9.0. Only about 0.5 ml 1.000 N NaOH was needed. A total of 2.000 ml of Pb solution and 10.00 ml of synthetic IWTP feed had been added. One drop of 1.000 N NaOH raised the pH from 8.84 to 8.89.
- Step 20. Monitored the pH for 20 min and was found to be stable at 8.85 ± 0.01 .
- Step 21. Sampled at timed intervals (Table 41) 10.00 ml of the slurry and centrifuged it immediately for 10 minutes. The supernatant was filtered through a 0.2 μ Aerodisc®

syringe filter. Exactly 6.00 ml of this filtrate was added to a sample vial with 1.000 ml of 6.0 percent HNO_3 then capped and mixed.

Step 22. The stirring was stopped. The blanket settled quickly to the bottom of the flask then continued to collapse over the next several minutes. The supernatant was clean and colorless.

Step 23. All of the nitric acid samples were analyzed for Cd, Cr, Cu, and Pb by ICP.

f. Screening of Alternative Precipitation Chemistries

Using the above procedure, but without the SCC blanket, additional precipitants were tested for a side-by-side comparison of impurity removal selectivity and completeness. These chemistries were described in the Part 1 and 2 Report⁽¹⁾. Table VI.E.4 summarizes the chemistries tested and the test results. The thio-polymer (Nalmet® 8702 and ISX) results were confounded with hydroxide precipitation since these polymers are only stable at $\text{pH} > 8$. Therefore, a nonpolymeric, pH stable thio precipitant (Xri-mercapto-s-triazine, TMT) was tested to identify which impurities were being removed by thio-precipitation versus those removed by only hydroxide precipitation. These test results are provided in Table 42.

APPENDIX G

RESULTS OF SELECTED BIOSLUDGE VOLUME REDUCTION TECHNOLOGIES FROM OC-ALC FUNDED (FOLLOW-ON) PROGRAM

APPENDIX G

RESULTS OF SELECTED BIOSLUDGE VOLUME REDUCTION TECHNOLOGIES FROM OC-ALC FUNDED (FOLLOW-ON) PROGRAM

1. Acid Hydrolysis of Biosludge

During the technical evaluation phase only batch experiments were conducted with OC-ALC IWTP#11 and IWTP#10. In order to operate a commercially viable system, it was necessary to determine operating parameters for a continuous flow tubular reactor system and additional batch tests were conducted to quantify the effects of operating temperature and nitric acid concentrations on the dewaterability of the treated sludge.

Batch tests were conducted at temperatures of 90 C, 120 C, and 180 C. The sludge dewatering enhancement at the lower temperature was minimal, but the operation of the reaction at 180 C did not increase significantly the solids content of the product filter cake compared to the 120 C reaction. Thus, an operating temperature of approximately 120°C and higher is required to have beneficial impacts.

The effects of nitric acid concentration on solids reductions and enhanced filterability/dewatering were tested by 180 C batch reactions. Even with no acid the results indicate that the quantity of solids was decreased by 34 percent, and the solids content in product filter cake was increased from 9.8 percent for untreated IWTP#11 to 32.4 percent. The reduction in filter cake weight compared to that of the untreated sludge was 80.2 percent

($100 \times \left(1 - \frac{(100-34)}{100} \times \frac{100}{32.4} \right)$). Increase of the acid concentration improved the solids

elimination from 34 percent without acid to 42 percent at a concentration of 1.75 percent acid, and a 61 percent reduction in waste solids with a 3.5 percent acid concentration. The overall reduction of wastes is improved from 80.2 percent without acid to 90.2 percent at 3.5 percent acid.

Continuous testing in a tubular reactor was conducted to evaluate the effects of process configuration, residence time, and acid concentration on the solids reduction and

filterability/dewatering of the treated material. Residence time effects were - 1) residence time beyond approximately 6 minutes has little effect on solids reduction, and no benefit for filterability/dewatering, 2) although the filterability of the treated sludge was significantly improved over the untreated feed material, it wasn't as good as batch tests at the same reaction conditions because of shearing of the solids by high shearing conditions during sludge passage through the pressure let-down orifice and the sludge pump (confirmed by a simulated shearing experiment that reduced filterability so that filter cake solids content was reduced from 42 percent for the unsheared product, compared to 8.6 percent for the sheared product solution. The shearing was partially eliminated by reconfiguration of the reactor pressure let-down to operate on the gas phase of the product. As was observed in the batch testing, enhanced filterability was realized even in the absence of acid addition, and the filterability is enhanced with increasing acid concentration, although, the filterability of solids was still not as good as comparable batch tests.

2. Wet Air Oxidation

US Filter/Zimpro, Inc. (Rothschild, Wisconsin) was contracted to run a set of design experiments to determine the operational conditions for their process. Their batch tests were conducted at 190 C, 200 C and 210 C at 10 and 30 minutes to minimize specific resistance of the treated sludge. The untreated sludge had a specific resistance of $925 \times 10^7 \text{ sec}^2/\text{gram}$ (at 10 psi, equivalent to $2500 \times 10^7 \text{ sec}^2/\text{gram}$ at 25 psi) and the reactions that were run at temperatures of 190 C and 200 C with 10 to 30 minute residence times reduced the specific resistance of the sludge to the range of $10 \times 10^7 \text{ sec}^2/\text{gram}$ to $14 \times 10^7 \text{ sec}^2/\text{gram}$, which is a very low resistance (these values are equivalent to about $35 \times 10^7 \text{ sec}^2/\text{gram}$ at 25 psi, as a reference, compare these values to WR-ALC sludge IWTP#2, which gave at best $81 \times 10^7 \text{ sec}^2/\text{gram}$). Further tests at 210 C at 10 and 30 minutes decreased the specific resistance further, to $7.6 \times 10^7 \text{ sec}^2/\text{gram}$ and $4.8 \times 10^7 \text{ sec}^2/\text{gram}$ respectively.

COD destruction increased with temperature and holding time from 13 percent at 190 C for 10 minutes to 29 percent at 210 C for 30 minutes. The quantity of solids in the sludge was reduced in a similar manner by 16 percent to 19 percent, mostly as a result of destruction of 27 percent to 32 percent of the organic material in the sludge. Dissolved COD (in filtrate) was not

reduced at all in these experiments, though a small increase in BOD (from 1 percent to 1.1 percent) was observed.

Because of the great reduction in specific resistance of the sludge, that was achieved by the 210 C reaction when carried out for 30 minutes, US Filter/Zimpro chose these conditions for testing of repeatability. The gas analysis performed for these test runs indicated a hydrocarbon concentration of 1580 ppm. The hydrocarbon was released by the formation of volatile organic molecules during treatment. Therefore, application of this technology will require treatment of the product gas prior to venting.

Filtration tests of the sludge treated at 210 C for 30 minutes resulted in a filter cake with a remarkable solids content of 74 percent. 72 percent of the cake solids were inorganic material. When both the solids elimination and the filtration results are combined, the waste reduction is 89.8 percent, within the range found for acid hydrolysis. If the actual solids content achieved in application is 55 percent (as suggested by the vendor) then the final waste reduction is 86.3 percent.